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LEACHING OF DISSOLVED ORGANIC CARBON AND SELECTED INORGANIC CONSTITUENTS FROM SCRAP TIRES

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LEACHING OF DISSOLVED ORGANIC CARBON AND SELECTED INORGANIC CONSTITUENTS FROM SCRAP TIRES

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ABSTRACT

An environmentally friendly method for the disposal of scrap tires is currently unavailable; as a result, ultimate disposal of used vehicle tires continues to be a major challenge around the world. In the United States (US), during the past two decades, scrap tires have been generated at the rate of approximately one tire per person per year (i.e., approximately 290 million new scrap tires every year). It is estimated that there are currently 2 billion tires stockpiled in the US. Due to various problems involved in the disposal of scrap tires, different alternatives for recycle and reuse have been examined; however, one concern is the leaching of different tire constituents (organic and inorganic) with time, and their subsequent potential harmful impacts on the environment.

The main objective of this study was to perform a systematic investigation to examine the leaching of dissolved organic carbon and selected inorganic constituents from crumb rubber and tire chips under different water chemistry conditions: at three different pH values (4.0, 7.0 and 10.0) in distilled and deionized water, and in the stimulants of acidic rain water (pH 3.0), hard groundwater (pH 8.3) and soft groundwater (pH 6.3) These are the water chemistry conditions that are likely to be encountered during scrap tire (crumb rubber or tire chips) reuse applications. One hundred grams of crumb rubber (8x14 mesh size) or tire chips (1"×1", 2"×2", 4"×2" and 6"×2") were soaked and mixed in each leaching solution with a solid to solution ratio of 1:20 at room temperature for one month period. Samples were periodically collected and analyzed for selected inorganic constituents (sulfur (S), zinc (Zn), cadmium (Cd), chromium (Cr),

arsenic (As), potassium (K), phosphorus (P), sodium (Na), manganese (Mn), iron (Fe), calcium (Ca), magnesium (Mg), aluminum (Al), copper (Cu), lead(Pb), selenium (Se), molybdenum (Mo) and nickel (Ni)), dissolved organic carbon (DOC), ultraviolet absorbance at 254 nm (UV_{254}) and dissolved nitrogen (DN). Toxicity Characterization Leaching Procedure test was also performed to assess the toxicity of the leachates.

Results showed that the best condition for using scrap tire chips in environmental reuse applications was around the neutral pH conditions. Leaching of dissolved organic carbon and selected elements was minimal around the neutral pH values. pH was a more important parameter than conductivity of the solution in controlling the leaching of DOC and selected elements from scrap tires. The changes in conductivity did not have a significant impact on the leaching of organics or inorganics. When tire chips were exposed to acidic conditions, Fe by far was the most significant metal leaching from tires at very large quantities (up to ~800 mg/ 100 g tire). The presence of organics significantly increased the Fe concentrations in water (e.g., ~ 20 mg/L at pH 4) above its solubility. Mn was the second metal observed leaching at acidic conditions; however at amounts (2-5 mg/ 100 g tire) significantly lower than Fe. When the tire chips were exposed to basic conditions, the leaching of DOC significantly increased (reaching 27 mg/ 100 g tire). For crumb rubber, leaching of DOC reached up to ~120 mg/ 100 g tire, indicating that organic components in tires are more prone to leaching under basic conditions. Under the basic conditions, the leaching of inorganics, including Fe (<1 mg/ 200 g tire) was significantly lower. As, Cd, Cr, Cu, Mo, Se, Ni and Pb were always below the detection limits for all conditions tested during one month of leaching experiments.

The $SUVA_{254}$ values of the leaching solutions remained in the range of 1.5 to 3.0 L/mg-m during the experiments. A gradual increase in the $SUVA_{254}$ values after the first week was observed, indicating an increase in the fraction of aromatic carbons leaching from the tires over time. The presence of some aromatic compounds in the leachate solutions was confirmed with gas chromatograph coupled with tandem mass spectrometer scans. Some of these compounds (e.g., aniline, benzothiazole, benzothiazolone) have been also reported in previous studies.

Analysis of DOC leaching data showed that the mass of DOC leached during the first 12 hr consisted of 40-50% of the leaching during the first week and 20-25% of the leaching during the four weeks of experiments. Although the cumulative DOC mass leached from tires depended on tire size and leaching solution, the leaching rate remained constant regardless of tire type and leaching solution composition. Analysis of leaching rate of four metals (Zn, Fe, Al, Mn) at acidic conditions showed a rapid initial leaching rate for Zn, followed by a slower but constant rate, while there was a constant rate of leaching for Fe, Mn and Al from the beginning of the experiments without showing any sign of slowing down. This observation was attributed to the release of the Zn from the rubbery portion of the tires due to the relatively similar leaching patterns observed for DOC and Zn. On the other hand, Fe, Al and Mn are probably coming from the wires in tire chips and showed a continuous and constant rate of dissolution.

Crumb rubber showed significantly higher degree of leaching than tire chips for all detected constituents except Fe, since the main source of the iron in tire chip was the wires that were removed prior to preparing the crumb rubber. Among the tire chips that

were within the particle size range of practical applications, leaching from 1"×1" size tire chips, in general, was higher than the other particle sizes. The difference in leaching among other particle sizes (2"×2", 4"×2" and 6"×2") was relatively small or negligible for most of the parameters monitored.

DEDICATION

I would like to dedicate this thesis to my family,

relatives and all friends for their continuous

love and support.

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LIST OF ABBREVIATIONS

ARTS	Asphalt Rubber Technology Service
BET	Brunauer-Emmett-Teller
DDW	Distilled and De-ionized Water
DN	Dissolved Nitrogen
DOC	Dissolved Organic Carbon
GC/MS/MS	Gas Chromatograph coupled with tandem Mass Spectrometer
GW	Ground Water
HDPE	High-density Polyethylene
ICP	Inductively Coupled Plasma
ICP-OES	Inductively Coupled Plasma with Optical Emission Spectrometry
MCL	Maximum Contaminant Level
MtBE	Methyl tert-butyl ether
NPDWR	National Primary Drinking Water Regulations
NSDWR	National Secondary Drinking Water Regulations
PAH	Polyaromatic Hydrocarbons
SBR	Styrene-Butadiene Rubber
SC	South Carolina
SCDHEC	South Carolina Department of Health and Environmental Control
$SUVA_{254}$	Specific Ultra Violet Light Absorbance at 254 nanometers
SVOC	Semivolatile Organic Compounds
TCLP	Toxicity Characterization Leaching Procedure
TPH	Total Petroleum Hydrocarbons
US	United States
USEPA	United States Environmental Protection Agency
UV_{254}	Ultra Violet Light at 254 nanometers
VOC	Volatile Organic Compounds

CHAPTER ONE

INTRODUCTION

An environmentally friendly method for the disposal of scrap tires is currently unavailable [Liu et al., 1998]; as a result, ultimate disposal of used vehicle tires continues to be a major challenge around the world. In the United States (US), during the past two decades, scrap tires have been generated at the rate of approximately one tire per person per year (i.e., approximately 290 million new scrap tires every year). It is estimated that there are currently 2 billion tires stockpiled in the US [Propovic, 2000]. A study conducted by the US Environmental Protection Agency (USEPA) indicated that 77.6 percent of the scrap tires accumulate in landfills, stockpiles and other illegal dumps. The remaining is used for energy generation (10.7 percent), recycling (6.7 percent) and export (5.0 percent) [EPA, 1991].

Tire disposal problems can cause serious environmental problems. Catastrophic fires and insect breeding are the two major health and environmental hazards associated with tire stockpiles [Liu et al., 1998]. Tire pile fires are dangerous, pose serious environmental problems, and are expensive to clean up afterwards. Tire fires emit clouds of noxious black smoke, carbon black, volatile organics, semi-volatile organics, polynuclear aromatic hydrocarbons, oil, sulfur oxides, nitrogen oxides, carbon oxides, and airborne particulates, such as arsenic, cadmium, chromium, zinc, iron, lead [Downs et al., 1996; Liu et al., 1998]. Another major problem is the shape of a tire that allows

accumulation of rainwater. This creates an ideal breeding habitat for mosquitoes carrying serious diseases [Manchon-Vizuete et al., 2004]. In addition, disposal of scrap tires in landfills has important challenges because they are non-biodegradable and bulky, they do not readily compact, and they may float to the surface after burial [Liu et al., 1998].

Due to voluminous production and various problems involved with the disposal of scrap tires, different alternatives for recycle and reuse have been examined [STMC, 1997]. There are three basic approaches to address the scrap tire problem: waste reduction, recycling, and resource recovery. This includes size reduction, devulcanisation, rubber reclamation, and pyrolysis. There are also several recycling options such as, use of scrap tires in highway constructions, in reefs, as barriers, adsorbent media, and incineration for energy production [Amoozegar and Robarge, 1999]. Many of these methods are energy demanding and costly. In addition, they can solve only a small fraction of the tire disposal problem.

In many reuse applications, especially during the direct use of tires (e.g., crumb rubber and tire chips) in the environment, one major concern is the leaching of different tire constituents (organic and inorganic) with time, and their subsequent potential harmful impacts on the environment. A typical tire structure includes synthetic rubber, natural rubber, sulfur and sulfur compounds, silica, phenolic resin, oil (aromatic naphthenic, paraffinic), fabric (polyester, nylon, etc.), petroleum waxes, pigments (zinc oxide, titanium dioxide, etc.), carbon black, fatty acid, inert materials, and steel wire [RMA, 2009]. As a result, the inorganic constituents in the leachates may include some heavy metals and sulfur, while organics are expected to consist of polyaromatic hydrocarbons

(PAHs) used in the rubber as a softener or filter [Wik and Dave, 2005]. A comprehensive understanding of leaching from tires is critical before developing direct application alternatives for waste tires as fillings, sorbents and possibly construction materials. Therefore, the main objective of this study was to perform a systematic investigation to examine the leaching of selected inorganic constituents and organics from tire crumb and tire chips under different water chemistry conditions. In addition, the project sponsor, the Asphalt Rubber Technology Service (ARTS) and South Carolina Department of Health and Environmental Control (SCDHEC), had a special interest to further understand leaching from scrap tires. The research was designed to characterize and quantify the leachate composition in aquatic environments that are expected to be encountered during tires (crumb or chips) reuse applications. Different sizes of tire chips were soaked in representative aqueous solutions, and the leachates were monitored for selected inorganic and organic constituents.

CHAPTER TWO

LITERATURE REVIEW

The main objective of this chapter is to provide a summary of the literature regarding the leaching from scrap tires. It should be noted that an important fraction of the literature on this topic has been mainly published in reports prepared for various agencies and magazine articles. However, some peer-reviewed articles published in journals were also found and included in this review.

By definition a scrap tire is a solid waste including any unwanted or discarded tire (regardless of type/size) that has been removed from its original purpose. In this manner, a tire which is no longer wanted to be used for its original purpose and has been disposed is recognized as a scrap tire. Consequently, scrap tires include all whole scrap tires and/or pieces of tires [OhioEPA, 2007].

Ultimate disposal of scrap tires continues to be a challenge for the environment. Although advances in the design and manufacturing of tires have resulted in products that are safe, durable, wear resistant and long lasting, these important qualities have also created important disposal challenges [Zelibor, 1991]. The disposal problems along with the generation of scrap tires at a fast rate (i.e., approximately 290 million new scrap tires every year) have resulted in the accumulation of scrap tires in large quantities. It is estimated that there are currently 2 billion tires stockpiled in the US [Propovic, 2000]. As mentioned previously, these stockpiles pose significant environmental and health hazard.

Therefore, there is great need for developing new solutions that will use large quantities of scrap tires thus preventing their accumulation.

Structure and Components of Tires

Most people think that tires are made of mostly rubber; however, automobile and truck tires are, in general, a complex combination of hydrocarbons, metals and minerals. There are many constituents that go into the manufacturing of a tire with the principal ingredient being either natural virgin rubber, synthetic rubber or recycled tire rubber [Sonti et al., 2003]. Automobile tires are mostly made of artificial rubber (Styrene and Butadiene copolymers), while truck tires typically have natural rubber as the main constituent [O'Shaughnessy and Garga, 2000]. Other materials in tires include steel, nylon, polyester, rayon, carbon black, fiberglass, aramid and brass. In addition, one of the most important components of a tire is its casing, which is the woven fabric that provides the shape, houses the inner tube, and it is the surface on which the rubber tread is vulcanized [Sonti et al., 2003].

Styrene–butadiene rubber (SBR) is the major component used in the manufacturing of automobile tires. Three parts of butadiene and one part of styrene are polymerized to form SBR (Figure 2.1). Other tire rubbers used are natural rubber (cis-polyisoprene), synthetic cis-polyisoprene, and cis-polybutadiene [O'Shaughnessy and Garga, 2000]. Some of the other chemicals which are added to rubber during the manufacturing of tires include: carbon black to strengthen the rubber and increase abrasion resistance; extender oil (a mixture of aromatic hydrocarbons) to soften the

rubber and increase its workability [Mastral et al., 2000]. The SBR is then cross-linked by sulfur linkages to improve its strength therefore the duration time of usage is increased. This is known as the vulcanization or cross-linking process [Cummings, 1998].

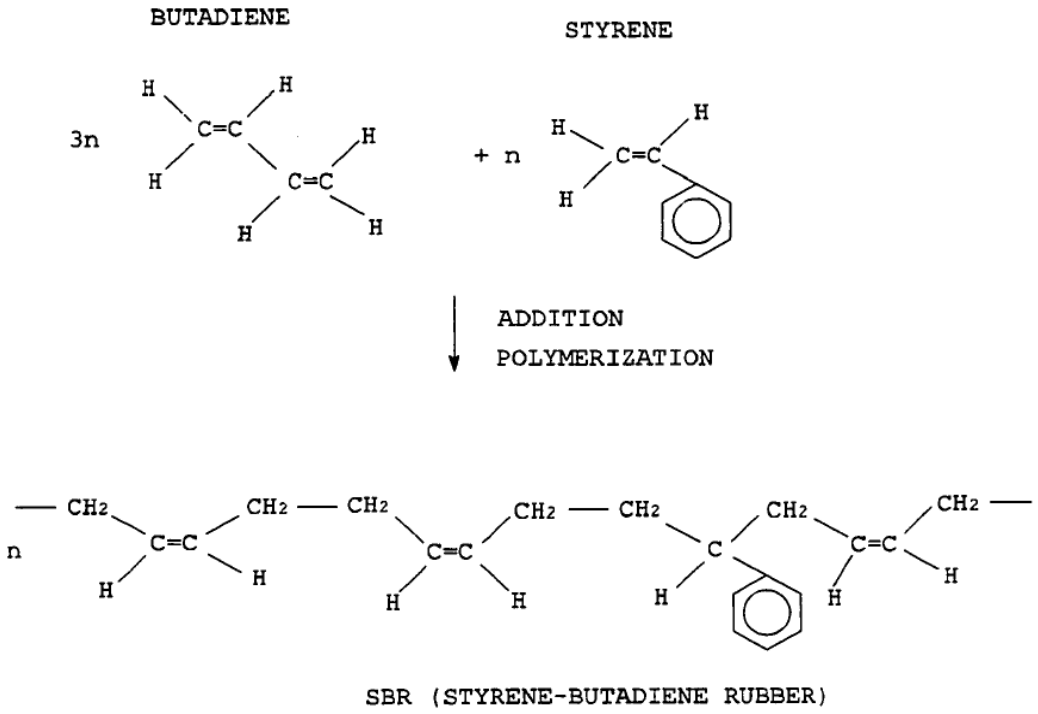


Figure 2.1: SBR polymerization schematic [Cummings, 1998]

Apart from the chemicals, several different additives are also used depending on the tire type. The most common additives and their roles on the process are listed below:

- Calcium oxide is used for improving the strength and the durability.
- Zinc oxide and titanium (IV) oxide are both used for speeding the vulcanization process up.

- Copper (II) oxide is the bonding agent to aid the steel belt adherence to the SBR.
- The zinc oxide, stearic acid, and an organo-sulfur accelerator are used to aid in the vulcanization process and enhance the physical properties of rubber.
- Antioxidant and some other additives are also added to prevent deterioration of the rubber complex. Other elements in the tire composition include iron and titanium from the steel belts and sulfur from the vulcanization or cross-linking process. Tires also contain very small amounts of silicon, aluminum, magnesium, sodium, potassium, and phosphorus [Cummings, 1998].

The weight percentage of major components in car and truck tires are shown in Table 2.1.

The rubber portion of a tire contains mostly carbon (88%), followed by hydrogen (8%), oxygen (2%), sulfur (1.5%) and some nitrogen (0.5%). Although most of the tires manufactured today are primarily steel-belted radial ply type, other types of tires are also available. Table 2.2 depicts the differences in various types of tires [Cummings, 1998]. A typical composition (by weight) of the ash fraction is given in Table 2.3.

Table 2.1: The tire components by weight (%) [RMA, 2009]

Material	Density (ton/m^3)	Car/Utility (%)	Truck/Lorry (%)
Rubber/Elastomers*	0.91	~41	~41
Carbon Black and Silica	2.3	~28	~28
Metal	7.6	~15	~15
Textiles, Additives, and Others	N/A	~17	~17
Estimated Average Density (ton/m^3):		1.25	1.28

N/A: Not Available.

*: Truck tires contain more natural rubber than synthetic rubber as compared to car tires.

Table 2.2: Analysis of various tires by weight (%) [Cummings, 1998]

Type	Ash	S	C	H	N	O
Fiberglass	11.7	1.29	75.8	6.62	0.2	4.39
Steel-belted	25.2	0.91	64.2	5.00	0.1	4.40
Nylon	7.2	1.51	78.9	6.97	<0.1	5.42
Polyester	6.5	1.20	83.5	7.08	<0.1	1.72
Kevlar-belted	2.5	1.49	86.5	7.35	<0.1	2.11

Table 2.3: Chemical composition of the ash by weight (%) [RMA, 1998]

Component	Passenger Tire	Truck Tire
SiO_2	22.96	23.83
Al_2O_3	17.11	3.65
TiO_2	10.14	0.13
Fe_2O_3	15.04	19.16
CaO	2.52	2.45
MgO	0.63	0.76
Na_2O	0.91	0.61
K_2O	1.00	0.90
P_2O_5	0.64	0.75
SO_3	4.20	5.94
ZnO	29.30	34.60
BaO	0.02	0.012
CdO	ND	0.001
Chlorine	ND	ND
Cr_2O_3	0.03	0.029
PbO	0.03	0.062
Flourine	ND	0.002
Se	ND	ND

ND: Not Detected.

Because various organic and inorganic chemicals are used in tire manufacturing, one major concern with scrap tires disposal and reuse is the potential leaching of those compounds, some of which are hazardous, to the environment. As a result, a number of studies have been performed to investigate the leaching from scrap tires.

Leaching from Tires

The removal of soluble material from a substance into a liquid is called "Leaching". A product or solution formed by leaching, especially a solution containing contaminants picked up through the leaching process is called "Leachate" [OhioEPA, 2007]. There have been different studies undertaken to examine leaching from tires. This section summarizes the review from these studies in three parts: Toxicity Characterization Leaching Procedure (TCLP), laboratory leaching tests and field studies. In these studies, scrap tires have usually been used in pre-cut forms with designated dimensions, and submerged into different solutions or used in several applications. The leachates were then analyzed for the compounds of interest (either organic or inorganic). It should be noted that in this section, detailed information about the reviewed studies such as, dimensions and type (car/truck) of tires, solid to liquid ratio, conductivity, pH and leaching cycle, were provided if specified in a study; otherwise, it was presented with a general terminology such as, scrap tires and leaching solutions).

TCLP Test

The TCLP is a test procedure developed by USEPA (Test Method 1311) to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes. TCLP is used to determine if a waste meets the definition of being a hazardous waste. The test simulates landfill conditions in which the percolating liquid often reacts with the solid waste in the landfill, and may pose public and environmental health risks because of the contaminants it absorbs. The TCLP analysis determines which of the contaminants identified by the USEPA are present in the leachate and their concentrations. The leachate should not contain any of the 40 contaminants above the limits outlined by USEPA (Table 2.4). Some studies have been conducted using the TCLP to assess the leachates from scrap tires. In this section, the research on TCLP test on scrap tires has been compiled.

Table 2.4: Regulated TCLP limits [EPA, 2009[b]]

EPA Hazardous Waste code	Contaminant	Regulated Level (ppm)
D004	Arsenic	5.0
D005	Barium	100.0
D018	Benzene	0.5
D006	Cadmium	1.0
D019	Carbon Tetrachloride	0.5
D020	Chlordane	0.03
D021	Chlorobenzene	100.0
D022	Chloroform	6.0
D007	Chromium	5.0
D023	o-Cresol	200.0
D024	m-Cresol	200.0
D025	p-Cresol	200.0
D026	Cresol	200.0
D016	2,4-D	10.0
D027	1,4-Dichlorobenzene	7.5
D028	1,2-Dichloroethane	0.5
D029	1,1-Dichloroethylene	0.7
D030	2,4-Dinitrotoluene	0.13
D012	Endrin	0.02
D031	Heptachlor	0.008
D032	Hexachlorobenzene	0.13
D033	Hexachlorobutadiene	0.5
D034	Hexachloroethane	3.0
D008	Lead	5.0
D013	Lindane	0.4
D009	Mercury	0.2
D014	Methoxychlor	10.0
D035	Methyl ethyl ketone	200.0
D036	Nitrobenzene	2.0
D037	Pentachlorophenol	100.0
D038	Pyridine	5.0
D010	Selenium	1.0
D011	Silver	5.0
D039	Tetrachloroethylene	0.7
D015	Toxaphene	0.5
D040	Trichloroethylene	0.5
D041	2,4, 5-Trichlorophenol	400.0
D042	2,4,6-Trichlorophenol	2.0
D017	2,4,5-TP (Silvex)	1.0
D043	Vinyl Chloride	0.2

One of the most comprehensive studies regarding TCLP test for tires was undertaken by Zelibor [1991]. In this study, the leachates from representative tires (grounded and ungrounded, cured and uncured, and truck and passenger tire samples) were investigated. The results indicated that TCLP regulatory limits were not exceeded for any tire or rubber compound. Most of the compounds were at trace concentrations which were 10 to 100 times lower than the TCLP regulatory limits or USEPA drinking water standard maximum contaminant level (MCL) values.

Another study was reported by Ealding [1992]. TCLP test was conducted on the representative 600 grams of tire chips. Instead of 20 times fold required by TCLP, a ratio of 1 to 2.84 (solid to liquid) was used in the experiments. The results indicated that the inorganic concentrations in the leachates were below the regulatory limits (Table 2.5), although the experimental condition was seven times more concentrated than the normal TCLP test.

Table 2.5: The concentrations of TCLP parameters reported by Ealding [1992]

Element	Concentration
Cd	1.55 ppb
Cr	2.8 ppb
Pb	19.6 ppb
Ag	<1.0 ppb
Ni	39.7 ppb
Al	148.0 ppb
Cu	83.0 ppb
Sn	<25 ppb
Fe	120.0 ppm
Zn	10.6 ppm
Mg	0.108 ppm
Ca	1.00 ppm

Downs et al. [1996] conducted TCLP test on two types of tires (steel belted and fiberglass) and the effect of washing the tires prior to testing. Their analysis involved both organics and inorganics. For the regulated TCLP metals, they detected barium (Ba), cadmium (Cd), chromium (Cr) and lead (Pb). The results indicated that the metals in the leachates were below the regulatory limits. The only regulated organic compound detected was 1,2-Dichloroethane and its concentration was below its regulatory limit. Also, the authors concluded that washing the tires with distilled and deionized water (DDW) prior to use had no significant effect on the concentrations of these compounds.

Al-Tabbaa and Aravithan [1998] investigated the use of natural clay-shredded tire mixtures as landfill barriers, and tested tire shreds by TCLP test for the use in landfills. The researchers reported only copper (Cu) and nickel (Ni) leaching. They had observed that the 1-4 mm size tire particles produced higher concentrations of the detected metals than the 4-8 mm size tire particles (Table 2.6). The results showed that the leachate contained 10 to 100 times lower concentrations than regulatory limits.

Table 2.6: TCLP test results from Al-Tabbaa and Aravithan [1998]

Tire Size	Cu (mg/L)	Ni (mg/L)
1-4 mm	0.24	0.59
4-8 mm	0.21	0.56

Considering the non-toxic classification of tire leachates from TCLP tests, several states have allowed the reuse of tires in different applications. In South Carolina (SC), the reuse of tires is outlined by “SC Solid Waste Policy and Management Act”. In September 1991, the Division of Onsite Wastewater Management under the Bureau of

Environmental Health at SCDHEC approved the use of tire chips as a substitute for gravel aggregate in the trenches of septic systems on a one-for-one volumetric basis. In December 1995, The Division of Onsite Wastewater Management revised the standards to require that tire chips must be between 0.5 and 4 inches in size with steel wires not protruding more than 0.5-inch from the sides of the chips. For use in septic systems, at least 90% of the tire chips must meet these revised standards.

In addition to TCLP tests, some additional toxicology testing were also preformed with tire leachates. Even though, these studies mostly focused on the toxicity of the leachate their results presented important key findings in terms of leaching from scrap tires. Gualtieri et al. [2005] investigated the toxicity of tire debris leachates. They used tire debris (10-80 μm) produced in laboratory from rubber. In the experiments, 50 and 100 g/L tire particles were used to produce leachates over the pH range of 3 to 7, and then the leachates were tested on *Raphidocelis subcapitata, Daphnia magna* and *Xenopus laevis* embryos to evaluate the toxicity of the leachate. Although the study focused mainly on the toxicity effect of leachate, their study is important for the demonstration of factors such as pH, and influence of size and particles aggregation on leaching. For instance, they had demonstrated that the leachate of smaller size tire chips were more toxic than bigger cut tire chips even though mass of bigger chips was twice more than small cut chips.

Azizian and Nelson [2003] investigated the leaching from ground tire rubber that was used in bituminous construction and as a crack sealer. DDW was used in the experiments with a 1:4 solids to liquid ratio. The researchers analyzed the organic and

inorganic constituents in the leachates, and also tested the toxicity of the leachates. They concluded that 50% of total leaching during one week occurred within the first 10 h of the experiments. Among the 20 inorganic constituents, only aluminum (Al) and mercury (Hg) were found at levels that were toxic to *Selenastrum capriconutum* and *Daphnia magna*. Also, they detected 10 organic contaminants in the leachates (Phthalaic anyhydryde, benzothiazole, decanoic acid, benaldehyde, glycine, quinoline, benzothiazole, hexadecanoic acid). Benzothiazole and 2(3H)-Benzothiazolone were also detected at concentrations that were toxic to *Selenastrum capriconutum* and *Daphnia magna*.

Laboratory Leaching Tests

Laboratory tests can be used to determine the types of contaminants that may leach from a scrap tire. Information obtained from these tests is useful in designing prior to a comprehensive field study to evaluate their environmental effects. Following studies reported in the literature investigated the leaching from scrap tires under laboratory conditions.

One of the most comprehensive laboratory studies on tire chips under various conditions was performed by Twin City Testing Corporation in 1990 to evaluate their performance for use in roadway sub-grades [Twin City Testing Corporation, 1990]. Leaching from scrap tires were tested under four scenarios. First, the pH of leaching solution was adjusted to 3.5 with acetic acid. In the second test, the leaching solution was maintained at pH 5.0. Third scenario involved using a 0.9% solution of sodium chloride

as the leaching solution to simulate the possible effects of road salt on the tires, and the fourth leaching solution was with a mixture of ammonium hydroxide and ammonium acetate solution at pH 8.0. Leachates from the waste tires were analyzed for the presence of organic compounds. Organics analysis included total petroleum hydrocarbons (TPHs) and PAHs. PAHs and TPHs were found to be most leachable under basic conditions. Leachates were also analyzed for the presence of inorganics including, Al, Ba, Cd, Cr, Pb, Hg, arsenic (As), calcium (Ca), iron (Fe), magnesium (Mg), sulfur (S), selenium (Se), silver (Ag), stannum (Sn), and zinc (Zn). It was found that highest degree of metal leaching from tire chips occurred under acidic conditions. Figure 2.2 illustrates the summary of findings from the study conducted by Twin City Testing Corporation.

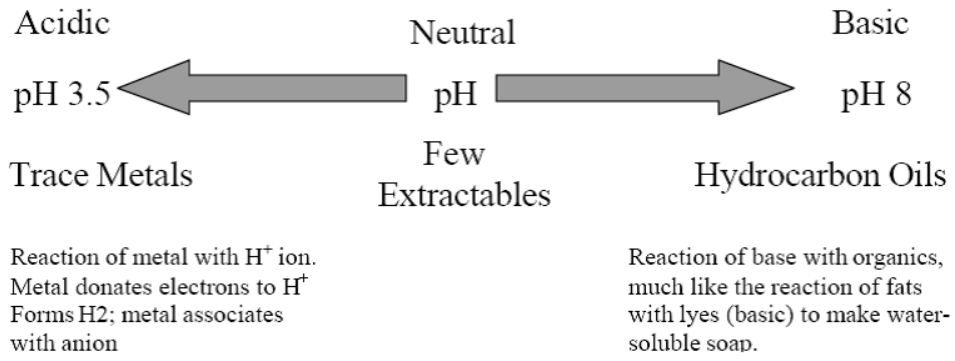


Figure 2.2: Illustration of test results [Twin City Testing Corporation, 1990]

Another comprehensive study was conducted by Lerner et al. [1993]. First, tire chips smaller than 0.5"×0.5" were tested in batch experiments using two leaching solutions with pH levels of 2.1 and 12.1 for 38 days. The results showed the presence of benzene, toluene, m/p-xylene, 1,2,3-trimethylbenzene, and dimethyl phthalate in the

leaching solutions. For the inorganic constituents, only As was found at concentrations higher than the controls. Then in a second set of experiments, three different sizes of tire chips (1"×1", 2"×2", 4"×4") were subjected to nine different aqueous solutions with three pH levels of 5.4, 7 and 8.6, and each pH with three total dissolved solid values of 100, 500, and 2,500 mg/L for a contact time of 91 days. Toluene, m/p xylene, o-xylene, ethylbenzene, 2-ethyltoluene, propylbenzene, 1,2,3-trimethylbenzene, and 1,2,4-trimethylbenzene were detected in leachates. Only As and Zn were consistently higher than the detection limits in the leachates. No Se was detected in any of the leachates, but Cd, Cr, and Pb were often detected in trace concentrations. The researchers concluded that organic compounds and metals leached from tire chips, and indicated that the majority of compounds identified in the study were used in the manufacturing of tires. Lerner et al. [1993] found that pH and electrical conductivity had little to no impact on leachability of chemicals from tire chips, which was not consistent with the observation at the Twin City Testing Corporation study, summarized previously. The size of tire chips affected the leaching of organic compounds. With the decreasing tire size, the degree of leaching increased. They also concluded that tire chips appeared to drive the pH of the leachate from acidic and neutral toward alkaline conditions.

Downs et al. [1996] investigated the long term leaching from a mixture of 3"×3" tires (steel belted and fiberglass). Eight reactors were set up including three reactors for three types of soils (till, clay and peat), three reactors with tire chips and one of the soil type, and two reactors, one with washed tire chips and other with unwashed tire chips. Reactors were filled up with DDW as the leaching solution, then they were sealed and

held (no mixing) at ambient temperature (15-20ºC) for a period of ten months. Ba, Cr, Fe, Zn and manganese (Mn) were detected and Fe and Mn exceeded their MCLs listed in National Secondary Drinking Water Regulations (NSDWR). However, Ba, Cr, and Zn levels were below their corresponding MCLs. It was also observed that Ba, Cr, Cu, Fe, Pb, Mn, and Zn in soil samples were increased. Some of the organic compounds detected were: 4-acetyl-morpholine, 2(3)-benzothiazolone, aniline, benzenepropanoic acid, benzothiazole, benzoic acid, bromomethane, benzene, trichloroethene, toluene, cis-1,2-dichloroethene, bromodichloromethane, trichloromethane, naphthalene, and 1,1-dichloroethene.

Spagnoli et al. [2001] evaluated whether tires would be a source of organic and metal contamination in groundwater when used in a septic system. They tested the leachability of tires in a wastewater to simulate the water in a typical septic tank. Researchers compared new tires with old tires, and used stone as control. Leachates were characterized for metals, Volatile Organic Compounds (VOCs), and Semivolatile Organic Compounds (SVOCs). Organic leaching potential of volatile and semi volatile compounds under submerged conditions was evaluated by measuring the concentrations of fifty-one selected VOC and SVOCs. The results showed the presence of no VOCs, while for SVOCs, only aniline and total creosols were detected. Fe, Mn, Zn, Ba, and Cu were detected in the leachate at concentrations higher than found in the control (i.e., stone). Results also indicated that As, Cu, Ni, and Pb concentrations in the leachate were negligible. Overall, metal concentrations appeared to be higher at acidic pH conditions.

In most of the cases, Fe and Mn were reported as the most leaching compounds, usually followed by Zn and Al.

O'Shaughnessy and Garga [2000] performed laboratory column tests on car tire chips embedded in inert Unimin quartz sand. Three different leaching solutions (DDW at pH 3.5 adjusted by sulfuric acid, at pH 6.5 and at pH 9.5 adjusted by sodium hydroxide) were tested. They analyzed the leachate for a number of inorganic constituents and organic compounds. benzothiazole, (1,1-dimethylethyl)-2-methoxyphenol, 2,5-dibutylthiophene, 4-(2,2,4-trimethylpentyl)phenol, 2(3H)-Benzothiazolone, and 4-(2-benzothiazolythio)morpholine. Leaching of organic compounds from the tire chips decreased with the time. The inorganic analyses indicated an increase in Al, Fe, Zn, and Mn concentrations which, with the exception of Zn, exceeded their respective drinking water standards. On the other hand, leaching of the following elements from tires was relatively negligible: Ba, Cd, Cr, Pb, Se, Cu, Ca, Mg, sodium (Na), potassium (K), chloride, fluoride, and sulphate. All of the organic compounds analyzed were detected in the leachates. However, it was observed that the total leaching of organics decreased with each leaching cycle.

The two studies performed by Ealding [1992] and Sengupta and Miller [1999] focused only on the inorganic compounds leaching from scrap tires. Ealding [1992] investigated the leaching of metals from scrap tires under different pH conditions. The experiments were conducted from one hour to one year contact time, at pH values of 4.0, 7.0 and 8.0. Five hundred grams of shredded tires were placed in 2-3 liters of leaching solution in one gallon polyethylene containers. For pH 4.0, DDW with 0.5 N acetic acid

was used, for pH 7.0, a 0.9% sodium chloride solution was used to mimic the road salt effect, and for pH 8.0 solution, a mixture of 1% ammonium acetate and 0.5 N ammonium hydroxide was used. The experiments were conducted in the dark at a temperature of 70-80°F and containers were shaken continuously and leaching solutions were replenished weekly. Samples were collected periodically, filtered and filtrates were digested and analyzed for Al, As, Ba, Ca, Cd, Cr, Cu, Fe, Hg, Mg, Ni, Pb, Ag, Se, Zn and Sn. Some of the important findings from this study were that metals leached more readily under acidic conditions (pH 4.0). The most abundant metal in the leachate was Fe followed by Zn and Ca. Leaching of other elements was much less particularly at higher pH's. Although organics were not analyzed in that study, it was noted that at higher pH values, carbon black was extracted along with an oily material.

Sengupta and Miller [1999] investigated the use of 2-inch scrap tire chips instead of gravel in residential subsurface leaching fields. They initially investigated the pH effect by conducting batch experiments at pH 6.2 and 3.5. The solutions were filtered and acid digested for inorganic analysis. The results indicated that leaching of metallic constituents from tires increased with decreasing pH. In the second part of their study, they had conducted column experiments which were operated at pH 6.4 and 3.0. pH stayed constant for the column that was operated at pH 6.4, however, the effluent pH increased to 6.0 for the other column with an influent pH of 3.0. Samples were analyzed for inorganic constituents only. The data showed that Fe, Mn, chloride and sulfate leached the most. Since, all of these compounds that were listed in NSDWR, they concluded that tires were not likely to affect water quality in terms of compounds listed

in National Primary Drinking Water Regulations (NPDWR). They observed that metals leached continuously whereas chloride and sulfate showed a decreasing concentration profile with the increased volume of water passed through the column. Also, metals leached more with the decreasing pH.

Overall, some general observations from the laboratory studies reviewed in this section are:

(i) pH of the solution was driven to alkaline conditions by tires [Lerner et al., 1993],

(ii) an influence of pH on leaching from tires was observed in studies conducted over a pH range [Twin City Testing Corporation, 1990; Ealding, 1992; Sengupta and Miller, 1999], while the effect of pH and conductivity of the solution was not observed in one study [Lerner et al., 1993],

(iii) leaching of metals increased under acidic conditions [Twin City Testing Corporation, 1990; Ealding, 1992; Sengupta and Miller, 1999]. Fe and Mn were observed in most studies at high concentrations [Downs et al., 1996; Spagnoli et al., 2001; O'Shaughnessy and Garga, 2000; Sengupta and Miller, 1999], while Zn and Al were found at lower concentrations as compared to Fe and Mn [Lerner et al, 1993; Downs et al., 1996; Spagnoli et al., 2001; O'Shaughnessy and Garga, 2000; Azizian and Nelson, 2003]. Any other metals, if observed, their concentrations were usually at trace levels,

(iv) hydrocarbons leaching was observed more under basic conditions [Twin City Testing Corporation, 1990]. Different organic compounds were identified in

several leachates and most of the detected organics were linked to the compounds used in the manufacturing of tires, and

(v) an increase in leaching was observed with decreasing particle size [Lerner et al., 1993; Gualtieri et al., 2005].

Field Studies

Some researchers have investigated the leaching from tires in field studies. Typically, scrap tires were shredded and placed in trenches. Downgradient water and soil samples were monitored periodically for the compounds of interest.

Humhrey and Katz [1996] evaluated the water quality effects of tire shreds placed below the water table. Groundwater samples were collected from the upper gradient, within the trench, and downgradient. Samples were taken over a four-year period and analyzed for a range of metals, VOCs, and SVOCs. From the tested 82 VOCs, cis-1,2-dichloroethene, benzene, 1,1-dichoroethane, 4-methyl-2-prentanone, 1,1,1-trichloroethane, 1,1-dichloroethene, xylenes, toluene, trichloroethene, 2-butanone, chloroethane and acetone were reported to be released from tire shreds at trace levels. For compounds that are in NPDWR, the levels were well below their MCLs. Also, from the 69 SVOCs monitored, aniline, phenol, m-- and p-cresol, benzoic acid, N-nitrosodiphenylamine, benzothiazole, 2(3H)-benzothiazolone, 3-methylbenzenamine, di-n-butyl-phthate, cyclohexanol, 2,6-bis-(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione, 2,6-bis- (1,1-dimethylethyl)-2, 4-(2-benzothiazolythio)-morpholine, diethytoluamide, 3-methylbenzenamine, 1H-isoindole-1,3(2H)-dione, 4-(2-benzothiazolythio)-morpholine,

N-(1,1-dimethlyethyl)- formamide, butanoic acid, and isothiocyanato cyxlohexane were found in most of the samples. The following metals, As, Ba, Cd, Cr, Cu, and Pb, that are listed in the NPDWR were tested, and only Ba was found to be higher than the background concentrations. The following metals, Ag, Al, Fe, Mn, and Zn, in the NSDWR, were also tested. Elevated levels of dissolved Fe, Mn, and Zn were recorded, whereas there was no change in the concentrations of others. All of the selected inorganic constituents appeared to decrease in the downgradient. Another study conducted by Humphrey et al. [1997] was to assess the potential leaching of organic and inorganic chemicals from tire chips placed above the ground water table under roads in Maine. Initially, tire chips were placed below a section of a road, and groundwater samples were collected. Groundwater samples were analyzed for total dissolved Al, Ba, Ca, Cd, Cu, Cr, Fe, Pb, Mg, Mn, Se, Na, Zn, Cl, and sulfate. Except for Al, Fe, and Mn, the concentrations of individual cations and anions were similar to background groundwater concentrations. Later, drainage water samples were collected from the tire chip fill areas directly beneath the fill layers. In addition to metals, the leachate samples were analyzed for selected VOCs and SVOCs. The amount of organic constituents in the water samples were below the detection limit for the respective analytical procedures. For inorganics, the concentrations of Fe and Mn were consistently higher in the leachates.

Following studies also investigated the use of scrap tires in trenches or septic systems. O'Shaughnessy and Garga [2000] collected water samples from a drainage system installed below the tire-reinforced earthfill and analyzed for chemical composition. Field monitoring of the prototype test embankment constructed with tires

above the water table indicated that insignificant adverse effects on groundwater quality had occurred over a period of 2 years. Selected inorganic constituents included Ba, Cd, Cr, Pb, Se, F, Mn, Cu, Fe, Zn, Na, chloride, and sulfate. No significant concentration change was observed for any of the compounds. All of the compounds were well below their respective regulated limits (MCLs in either NPDWR or NSDWR). In this investigation, only one organic compound, namely 4-(2-benzothiazolythio) morpholine, was detected in one of three test sections and in two of seven sampling events.

A study conducted by University of Massachusetts [Sengupta and Miller, 2000] investigated the use of tires in trenches. Three trenches were constructed (two of scrap tires and one trench filled with gravel) and pits were lined with a geomembrane for the collection of effluent. The effluent was monitored for parameters such as, pH, conductivity, total alkalinity, biochemical oxygen demand, fecal coliform, total suspended solids, ammonium nitrogen, orthophosphate phosphorus, sulfate, chloride, Al, Mn, Cu, Cr, Fe and Zn. It was found that trenches with scrap tires did not leach any toxic metal or inorganic anion. The only compound that exceeded the NSDWRs MCL was Mn. Lerner et al, [1993] evaluated the use of tire chips in septic systems. An experimental septic system was operated for 101 days, one filled with 1"×2" size tire chips and one filled with commonly used gravel aggregate. Water samples were collected and analyzed for 46 compounds, 11 acidic compounds, 16 pesticides and SVOCs, and a series of VOCs. The results showed that there was no leaching of SVOCs. As for the VOCs, 1,3,5-trimethylbenzene and methyl isobuthyl ketone were found at low concentrations only in the samples from tire chip-filled trench, which were detected after a certain exposure

period. As for the inorganic elements, Cr, Pb, Sn, and Zn were detected at trace concentrations.

Also, Downs et al. [1996] investigated the use of tires in trenches in different types of soils (till, clay and peat). Groundwater samples were collected from the upgradient, trench and downgradient and samples were analyzed for metals, organics, biochemical oxygen demand, chemical oxygen demand, total organic carbon, alkalinity, pH, conductivity, chloride and sulfate. Field study results were consistent with their lab studies. Ba, Cr, Fe, Mn and Zn were detected and Fe and Mn exceeded their MCLs listed in NSDWR, whereas, Zn was within the regulatory limits. Ba and Cr were detected at trace concentrations. Some of the organic compounds detected were: 1,1-dichloroethene, (Z)-1,2-dichloroethene, 1,1,1-trichloroethane, benzene, toluene, naphthalene, phenol, p-creosol, 1H-Isoindole-1,3(2H)-dione, 2(3)-benzothiazolone, aniline, benzothiazole, butanoic acid, benzoic acid, and cyclohexanol.

Edil and Bosscher [1992] investigated the use of tires in embankments. They collected samples from a test embankment that was constructed with eight tire chip-filled cells. Two sources of scrap tires had been studied but no control section was used in their study. Fe, Zn, Mn levels at high concentrations (The compounds were within the MCLs of NSDWR); however, it was implied that they might had come from other sources.

The results of the field studies, although limited, indicate that the major concern is with the aesthetic water quality parameters such as Fe, Mn, Zn and Al [Humhrey and Katz, 1996; Humphrey et al., 1997; O'Shaughnessy and Garga, 2000; Sengupta and Miller, 2000; Downs et al., 1996; Edil and Bosscher, 1992]. None of the compounds

exceed their MCLs for NSDWR except for Sengupta and Miller's [2000] and Downs et al.'s [1996] field tests. Also, no significant concentration of other inorganic constituents has been reported. No major concern has been reported for the organics, few organic compounds have been detected and those organic compounds were at trace levels [Humhrey and Katz, 1996; Humphrey et al., 1997; O'Shaughnessy and Garga, 2000; Lerner et al, 1993; Downs et al., 1996].

CHAPTER THREE

RESEARCH OBJECTIVES

Considering the facts that (i) approximately 290 million new scrap tires are generated per year in the US, (ii) it is estimated that there are currently 2 billion tires stockpiled in the US, and (iii) 77.6 percent of scrap tires ends up in landfills, stockpiles and other illegal dumps, there has been a continuous effort for developing environmentally friendly, sustainable, and feasible solutions for reuse of tires. At the same time, there has been some concerns from the reuse of scrap tires, as documented in recent news stories (Appendix A), including potential leaching of organic and inorganic compounds into local water sources. Although some research have been conducted on this topic, as reviewed in the previous chapter, there is still much to learn about the leaching of organic and inorganic constituents from scrap tires.

The main objective of this study was to examine the leaching of selected inorganic constituents and organics from crumb tire and tires chips under representative water chemistry conditions. Specifically, this research investigated:

- ***The effect of aqueous chemistry on the leaching of organic carbon and inorganic constituents from tires***

  The effect of pH was examined in many previous studies. In this study, in addition to pH effect, leaching from tires was examined under simulated soft and hard groundwater as well as rainwater conditions. Therefore, a wide range of aqueous

chemistry conditions likely to be encountered in tire reuse applications and disposal scenarios were investigated. In addition, leaching under the TCLP condition was examined. Many times in the literature, the leaching of both inorganic and organic constituents were not examined during the same study. Therefore, this is the one of the few study in the literature simultaneously examining the leaching of organic and inorganics constituents from tires in a wide aqueous chemistry and the TCLP conditions.

- ***To examine the leaching of total dissolved organic carbon and dissolved nitrogen from tires***

  Most of the time, the emphasis in the literature was given on the leaching of some specific VOCs and SVOCs from tires. There is no study documenting the leaching of overall dissolved organics from scrap tires under different water chemistry conditions. Understanding the overall dissolved organic leaching is important because it will provide information about the magnitude of dissolved organics leaching, although as a surrogate measure, from scrap tires. The concentrations of these organics can be much higher than the amounts of VOCs and SVOCs detected at micro concentrations as reported in previous studies. Since they are in dissolved state, they are likely to enter to water sources or may get in contact with public, creating various concerns. In this study, leaching of non-volatile dissolved organic carbon (DOC) was monitored. DN was also monitored because it was possible to measure both DOC and DN in the same sample during analysis. The characteristics of dissolved organic leaching from tires were monitored by

ultraviolet absorbance at 254 nanometers (UV_{254}). In selected samples, the composition of organics in the DOC mixture was qualitatively scanned and identified using a Gas Chromatograph coupled with tandem Mass Spectrometer (GC/MS/MS).

- ***To quantify the leaching of organics and inorganic constituents from scrap tires as a function of time during one month period***

  Although leaching from tires has been investigated in the literature, the rate of leaching has not been quantified and has only been reported in one study. In this study, leaching from tires was monitored periodically for one month period to gain some insight to the rate of leaching from tires.

- ***To examine the effect of particle size on leaching***

  Although the effect of particle/tire chip size has been previously investigated, this study investigated all the objectives above in a wider particle/tire chip size range that are expected to be used in practical applications.

  Table 3.1 shows the experimental matrix conducted during this study.

Table 3.1: Experimental matrix

Leaching Solutions	Tire Chips				
	Crumb	1"×1"	2"×2"	4"×2"	6"×2"
pH 4.0*	✓	✓	✓	✓	✓
pH 7.0*	✓	✓	✓	✓	✓
pH 10.0*	✓	✓	✓	✓	✓
Rainwater (pH: 3.0)	✓	✓	✓	✓	✓
Soft GW (pH: 6.3)	✓	✓	✓	✓	✓
Hard GW (pH: 8.1)	✓	✓	✓	✓	✓
TCLP Test	✓	✓	✓	✓	✓

*: pH of DDW was adjusted by high purity HCl or NaOH.

CHAPTER FOUR

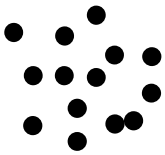
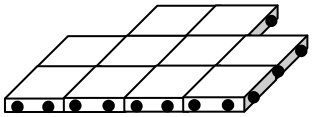
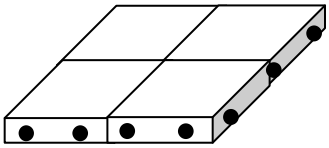
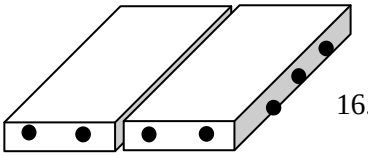
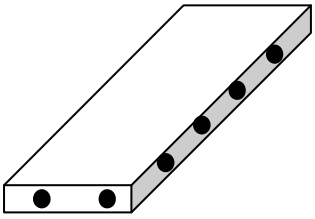
MATERIALS AND METHODS

Tire Chips

Scrap tires for this research were supplied by the ARTS Center at Clemson University. Tires were stockpiled after completing their purpose of use until taken for shredding. The tires supplied in the study were a mixture of car and truck tires (approximately 90% car and 10% truck tires). All the tire chips were uniformly cut by ARTS Center, and the experiments were conducted for four different particle sizes: 1"×1", 2"×2", 4"×2" and 6"×2" chips. The average thickness of tire chips was about 0.4 inches. The steel wires at the sides of the tires were cut before the experiments. This particle size range were selected to be consistent with "SC Solid Waste Policy and Management Act", in which for applications in septic systems tire chips must be between 0.5 and 4 inches in size with steel wires not protruding more than 0.5 inch from the sides of the chips. In addition to the tire chips, crumb rubber (14-8 mesh size) was also included in the matrix to examine the behavior of a tire chip pulverized at ambient temperature after the removal of wires.

Representative shapes and properties of tires used in the experiments are given in Table 4.1 and some pictures of tires chips before and after the leaching experiments are shown in Appendix B. All chips were rinsed with DDW prior to experiments in order to remove the apparent dirt, sand, grit and other foreign particles.

Table 4.1: Chip sizes, shapes and surface areas

Chip Size (inch)	Number of Chips in a Bottle	Chip Shapes	Top Surface Area[a] ($inch^2$/100g)	Side Surface Area[b] ($inch^2$/100g)	Total Surface Area[c] ($inch^2$/100g)
Crumb Rubber (8×14 US mesh)	≈68000[d]		N/A	N/A	BET[e] ≈149000 Theoretical[f] ≈4800
1"×1"	10		16.0	16.0	48.0
2"×2"	4		16.0	12.8	44.8
4"×2"	2		16.0	9.6	41.6
6"×2"	1		12.0	6.4	30.4

[a]: Tires chips were laid on a flat surface and the dimensions were measured to calculate the top surface area.
[b]: Side surface area of selected tire chips were measured and average values were reported.
[c]: The summation of measured of top, bottom and side surface areas of tire chips.
[d]: Approximate number of crumb rubbers in 100g estimated by counting crumbs in 0.5g, 1g, and 2.5g samples, and taking the average.
[e]: BET surface area was determined by analyzing crumb rubbers in the surface area analyzer.
[f]: Theoretical surface area was estimated by calculating the surface area of an average particle size (diameter of 1.9 mm) as a sphere and then multiplying by the number of crumbs.
N/A: Not Applicable.

Leaching Solutions

Leaching from tires was investigated under six different water chemistry conditions: in leaching solutions at pH 4.0, 7.0 and 10.0, and an acidic rain water, and hard and soft groundwater simulants. For the leaching solutions, pH of DDW was adjusted using high purity 0.25 M NaOH (Titristar Grade) or HCl (OmniTrace Grade for Inductively Coupled Plasma (ICP) analyses) without using any buffer. In Table 4.2, the concentrations of the constituents in the rainwater, hard and soft groundwater (GW) stimulants are shown. The compositions of the simulants were determined based on the reports literature [Hem, 1985; Drever, 1982; Kim and Aneja 1992]. The overall experimental matrix conducted during this project was provided previously in Table 3.1.

Table 4.2: The compositions of rain water and groundwater stimulants

Simulant	pH	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^{+} (mg/L)	K^{+} (mg/L)	HCO_3^{-*} (mg/L)	SO_4^{2-} (mg/L)	Cl^{-*} (mg/L)	SiO_2^{*} (mg/L)	Conductivity (μS/cm)
Hard GW	8.1	56.0	26.0	59.0	3.2	622	129.0	53.0	22.0	742
Soft GW	6.3	2.9	0.6	4.7	1.0	20	1.0	0.5	16.4	88.5
Acidic Rainwater	3.0	0.7	0.1	0.3	0.2	N/A	40.9	1.9	N/A	314

*: All parameters except these three were measured. These three components were in the simulant recipe but their final concentrations in the simulant solutions were not quantified.
N/A: Not Available.

Leaching Experiments

The crumb tires or tire chips were soaked in each leaching solution at a constant solid and solution ratio (mass ratio of 1:20) and room temperature (22±2ºC) under the same mixing conditions on a rotary thumbler. Since the tire mass was kept constant at 100 g in all experiments, different numbers of tire chips were placed in 2.5-L wide mouth amber bottles with Teflon lined cap for the experiments depending on particle size and filled with 2 liters of leaching solution (Table 4.1). One soaking cycle continued for one week. During this period, pH of the leaching solution was recorded and adjusted daily to its initial value by using high purity 0.25 M NaOH or HCl. 30 mL of samples were removed, after each sampling the same volume of fresh leaching solution was added back to reactors. Samples were analyzed for inorganic and organic constituents. At the end of one week period, tires were separated by filtration, and leaching solution was replaced with a fresh solution in order to maintain high concentration gradient for leaching. This one week soaking procedure was repeated for one month, by the time leaching significantly slowed down. Leaching experiments were run in duplicates; however, if there was a deviation more than 20% between the total mass of a constituent leached from two samples, and an additional leaching experiment was conducted.

Sampling Method

The bottles were sampled periodically (Regular sampling days: 1, 3, 5, 7, 8, 10, 12, 14, 15, 17, 19, 21, 22, 25, and 28; for selected leaching solutions additional samples were taken on days 0.5, 2, 4, and 6). Each sample was filtered with plastic syringes (BD

30mL latex free and poly lined syringe) through a pre-washed 0.45-μm membrane filter (Pall Corporation, acrodisc syringe filters with Supor membrane (hydrophilic polyethersulfone)) into two separate vials: high-density polyethylene (HDPE) vials for inorganic analyses which were acidified with high purity nitric acid (Omnitrace Grade for ICP analyses), and borosilicate amber glass vials for DOC, DN and UV_{254} analyses. In order to maintain the solid to liquid ratio constant in the bottles, after each sampling the same volume of fresh leaching solution was added back to the reactors. Since 30 mL of sample was taken daily, there was no significant dilution effect on the leachate after the replacement of leaching solution.

TCLP Test

TCLP test was performed following EPA's method 1311. The method involved extraction of scrap tires with an amount of extraction fluid equal to 20 times the weight (100 g of tires : 2 L of extraction fluid). The extraction solution consisted of 5.7 mL of glacial acetic acid and 64.3 mL of 1 N NaOH per 1 liter with a pH of 4.93 ± 0.05. Size reduction was not employed to the tires in order to monitor the size effect. Tires and extraction solution were placed in a 2.5 L amber borosilicate glass with Teflon lined cap, and agitated (end-over-end fashion) at 30 rpm for 18 hours. At the end of contact period, samples were taken with (BD 30mL latex free and poly lined syringe) and filtered through 0.45-μm membrane filters (Pall Corporation, acrodisc syringe filters with Supor membrane (hydrophilic polyethersulfone)), and acidified with high purity nitric acid and analyzed with ICP-OES (Inductively Coupled Plasma with Optical Emission

Spectrometry) at Agricultural Service Laboratory in Clemson University (Table 4.4). Due to funding limitations in this study, only the inorganic constituents listed in Table 4.4 were monitored during the TCLP tests.

Analytical Methods

Analytical methods described in this section have already been available in Dr. Karanfil's research group from previous projects. The author of this thesis used these analytical tools to produce the experimental results presented in this document. Table 4.3 shows a summary of analytical methods used in this project. Each method was also briefly described after the table.

Table 4.3: Analytical methods and minimum reporting levels

Parameter	Unit	Measurement Method	Equipment	Minimum Detection Levels[a]
DOC[b]	(mg/L)	SM[c] 5310B High Temperature Combustion	TOC-V_{CSH}, Shimadzu Corp., Japan	0.10
DN[d]	(mg/L)		TNM-1, Shimadzu Corp., Japan	0.10
UV Absorbance[e1]	(abs)	SM 5910	Cary 50, Varian Inc., USA	0.003[e2]
pH		SM 4500-H^+	420A, Orion Corp., USA	±0.01[f]
Inorganic Constituents	(µg/L)	SM 3120B	ARCOS ICP-OES outfitted with axial plasma observation, Spectro Corp., Germany	Element Dependent (Table 4.4)

[a]: As reported by the manufacturer.
[b]: Reagent grade potassium hydrogen phthalate was used to prepare external standards. Precision ranged from 0.05 to 0.15 mg/L.
[c]: SM: Standard Methods.
[d]: Reagent grade potassium nitrate was used to prepare external standards.
[e1]: Measured at wavelength of 254 using a 1-cm cell.
[e2]: Photometric accuracy (absorbance units).
[f]: Accuracy (pH units).

Dissolved Organic Carbon

DOC was measured using a Shimadzu TOC-V_{CSH} high temperature combustion analyzer equipped with an auto-sampler. For DOC analysis samples were acidified by HCl. Acidified samples were purged for four minutes prior to analysis. DOC standards were prepared in the range of 0.2 to 15 mg/L from a 1000 mg/L stock solutions of potassium hydrogen phthalate. DOC samples were preserved by reducing the sample pH to less than 2 and refrigeration.

Dissolved Nitrogen

DN was measured using a total nitrogen analyzer (Shimadzu, TNM-1) equipped with the DOC analyzer. The same injection made for DOC analysis was also used in the DN determination. DN standards were prepared in the range of 0.4 to 10 mg/L from a 1000 mg/L stock solution of potassium nitrate.

UV Absorbance

UV absorbance was measured using a Cary 50 UV-Vis spectrophotometer (Varian). Samples were placed in a 1-cm quartz cuvette and measured at the wavelength of 254 nm. The spectrophotometer was blanked using the corresponding leaching solution of each experiment. Blank checks were performed every 10 samples, and the performance of the analyzer was monitored using total organic carbon standards.

pH

The pH values for samples were measured using SM 4500-H^+ pH electrode with an Orion 420A pH meter (Orion Corp., USA). The pH meter and electrode were daily calibrated using standard pH 2, 4, 7 and 10 buffer solutions.

Inorganic Constituents Analysis

Inorganic constituents were measured by Kathy Moore in Clemson University Agricultural Service Laboratory using Spectro ARCOS ICP-OES outfitted with axial plasma observation. Detection limits of the constituents are given in Table 4.4.

Surface Area Analysis

The surface areas and total pore volumes of crumb rubber samples were determined from nitrogen gas adsorption results. Nitrogen gas adsorption isotherms were volumetrically obtained in the relative pressure range of 10^{-6} to 1 at 77 K on a Micromeritics ASAP 2010 physisorption analyzer. Surface area was calculated from Brunauer-Emmett-Teller (BET) equation. The relative pressure range used for the BET calculation was 0.01 to 0.1. The adsorbed volume of the nitrogen near saturation point ($P/P_o = 0.98$) was used to determine the total pore volume. Triplicate results of randomly selected samples were used to determine the reproducibility of the data and the relative standard deviation of the BET surface area, and the total pore volume was lower than 10%. These characterization experiments were performed by Dr. Shujuan Zhang, who is a post doctoral research associate in Dr. Karanfil's laboratory.

Table 4.4: Detection limits of elements measured with ICP-OES

Element	Wavelength (nm)	Detection Limit (µg/L)
Ag	328.07	0.4
Al	167.08	0.05
As	189.04	2.0
B	182.64	0.5
Ba	455.40	0.03
Be	313.04	0.08
Br	154.06	30.0
Ca	396.84	0.03
Cd	226.50	0.2
Cl	134.72	50
Co	228.62	0.2
Cr	267.72	0.4
Cu	324.75	0.3
Fe	259.94	0.3
Hg	184.95	0.5
I	161.76	50.0
K	766.49	1.0
Li	670.78	0.04
Mg	279.55	0.01
Mn	257.61	0.03
Mo	202.03	0.5
Na	589.59	0.8
Ni	231.60	0.6
P	177.50	2.0
Pb	168.22	1.3
Sb	206.84	2.5
S	180.73	3.0
Se	196.09	2.5
Si	251.61	2.2
Sn	189.99	0.6
Sr	421.55	0.03
Ti	334.94	0.2
Tl	190.86	1.0
V	292.46	0.4
Zn	213.86	0.3

Elemental Analysis

Carbon, hydrogen, nitrogen, sulfur and oxygen contents of crumb rubbers were determined using Thermo EA 1112 CHNS-O. In order to dehumidify samples, crumb rubbers were stored in the desiccator. 0.1 mg of sample was combusted at 1,800 ºC in the presence of excess oxygen and combustion reagents. Samples were combusted completely and reduced to the elemental gases CO_2, H_2O, N_2 and SO_2. For the oxygen content, samples were pyrolyzed in a helium/hydrogen (95%:5%) atmosphere at 1,000 °C. The results were reported as weight fractions.

Dry Ashing

Ash content of the crumb rubber or tire chips was determined by placing a dehumidified sample in an open inert vessel and destroying the combustible portion of the sample by thermal decomposition using a muffle furnace. To facilitate the digestion, tire chips were cut to 0.5"×0.5" size. Ashing temperature was 550 °C and samples were left for 24 hours for complete combustion of the sample. The dried samples were weighed before and after the ashing. Mass difference was used to calculate the ash fraction.

Acid Digestion

Acid digestion was used to analyze the contents of tire ashes. The samples were digested using a high purity concentrated nitric acid over a hot plate until a light colored, clear solution was observed. Spiraled finger condenser was used to improve recovery.

Digested samples were let to settle overnight to remove insoluble material. Decanted samples were diluted and analyzed with ICP-OES at Agricultural Service Laboratory in Clemson University.

Preparation, Analysis and Identification of Organic Compounds

In selected samples, organics in the leaching solutions were extracted using a method available in Dr. Karanfil's research group. The goal here was to qualitatively identify some of the organic compounds in the leaching solution. A 20 mL of sample was extracted with 4 mL of methyl tert-butyl ether (MtBE) in the presence of 10 g Na_2SO_4 (for salting out effect) and 1 g of $CuSO_4$ (for facilitating phase separation). The extraction involved 30 min of solution shaking on a shaker table. The MtBE extract was analyzed with Varian 4000 GC/MS/MS equipped with Rtx®-5MS (RESTEK, 30m × 0.25mm × 0.25μm). The temperature program was set at 35°C for 4 minutes, 20°C /min to 285°C, and held for 1.5 minutes. The sample (10 μL) was injected in splitless mode. The carrier gas was ultra high purity helium with a flow rate of 1.0 mL/min. The injector temperature was set at 240°C to maximize volatilization of compounds and the transfer line temperature was 200°C. The MS was operated at automatic electron impact ionization mode with the following specifications: mass range from 40 to 400 m/z, 2 μScans averaged, target total ion current of 25,000 counts, max ion time of 30,000 μseconds, emission current of 25 μamps. The organic compounds were identified using the library provided by the Varian 4000 GC/MS/MS software.

CHAPTER FIVE

RESULTS AND DISCUSSION

The results obtained in this research will be presented in three sections in this chapter. The first section will provide the results for the characterization of scrap tire particles, which will be useful for examining the leaching behavior of tires. In the second section, the leaching from tires under different aqueous chemistry conditions will be discussed. The TCLP test results will be provided in the last section to discuss the potential toxicity of tires.

Characterization of Scrap Tires

In order to examine leaching from scrap tires, it is useful to examine their physical and chemical characteristics. This section will present a discussion of the characterization data collected for tire chips used in the experiments. Surface area, pore volume, elemental content and ash compositions were examined.

Surface Area and Pore Volume Analyses

Due to particle size requirements for nitrogen gas adsorption analysis, crumb rubber samples were used in the surface area and pore volume determinations. The average BET surface area and total pore volume of triplicate samples were 0.9596 ± 0.0573 m^2/g and 0.000733 ± 0.000055 cm^3/g, respectively (Table C.1). Measured BET

surface area indicated that surface of tires were very small and measured value was found within the range (0.059 – 3.5 m^2/g by N_2 adsorption for similar sized crumb rubbers) reported by previous studies [Holland et al., 1994; San Miguel et al., 2002]. Pore volume analysis indicating that the tires did not have appreciable pore volume by N_2 adsorption, which was consistent with previous researches [Holland et al., 1994; Manchon-Vizuete et al., 2004; Manchon-Vizuete et al., 2005; Bilgili et al., 2001]. This data suggested that leaching from tires could occur primarily from their external surfaces.

Elemental Analysis

For the elemental analysis, six crumb samples were analyzed (Table C.2). Since the elemental analyzer measures carbon, hydrogen, nitrogen, sulfur and oxygen of a sample, the remaining fraction was considered as ash fraction. The results from these two set analyses were compared and found to be consistent. Average values are presented in Table 5.1.

Table 5.1: Elemental analysis

Element	Weight Fraction (%)
Carbon	80.51 ± 3.78
Hydrogen	7.33 ± 0.18
Nitrogen	0.43 ± 0.08
Sulfur	1.06 ± 0.15
Oxygen	2.47 ± 1.64
Ash	8.21 ± 2.19

Several studies examined the elemental composition of different types of tires (Table 5.2). The data obtained in this study (Table 5.1) were consistent with previous

studies [Cummings, 1998; Manchon-Vizuete et al., 2005]. The results confirmed the presence of a high carbon content in the tire structure, which is consistent with the manufacturing process (SBR and carbon black) [Cummings, 1998; RMA, 1998]. Similarly, there is a significant fraction of hydrogen in the structure which is also related to SBR. During the polymerization step, the effect of sulfur addition is also reflected in the results. Different tire types have different sulfur contents simply due to integrity requirements. Oxygen was detected in all samples and the main source of oxygen was attributed to presence in organics, oxides in metals (such as, iron oxide, zinc oxide, titanium oxide), and textiles. There was also a small fraction of nitrogen detected. Even though, there is no addition of nitrogen reported during the manufacturing process, it may result from various organics and inorganics used in manufacturing process.

Table 5.2: Analysis of various tires by weight (%) [Cummings, 1998]

Type	Ash	S	C	H	N	O
Fiberglass	11.7	1.29	75.8	6.62	0.2	4.39
Steel-Belted	25.2	0.91	64.2	5.00	0.1	4.40
Nylon	7.2	1.51	78.9	6.97	<0.1	5.42
Polyester	6.5	1.20	83.5	7.08	<0.1	1.72
Kevlar-Belted	2.5	1.49	86.5	7.35	<0.1	2.11

Ash Content Analysis

The ash content of tire chips were determined by high temperature combustion of five independent samples of tire crumb and tire chips in a muffle furnace, and subsequent acid digestion of the ash. The results are presented in Table 5.3.

Table 5.3: Element content (mg/g)

Element	Crumb Rubber	Tire Chip
Al	2.216 ± 0.325	0.519 ± 0.219
As	ND	ND
Ca	1.717 ± 0.122	0.535 ± 0.112
Cd	0.004 ± 0.001	0.002 ± 0.000
Cr	0.003 ± 0.001	0.041 ± 0.022
Cu	0.036 ± 0.010	0.309 ± 0.143
Fe	1.401 ± 0.153	110.432 ± 56.093
K	0.415 ± 0.118	0.586 ± 0.383
Mg	0.291 ± 0.048	0.152 ± 0.020
Mn	0.016 ± 0.002	0.657 ± 0.142
Mo	ND	ND
Na	0.519 ± 0.182	0.311 ± 0.154
Ni	0.004 ± 0.001	0.045 ± 0.027
P	0.165 ± 0.003	0.165 ± 0.014
Pb	0.050 ± 0.013	0.036 ± 0.011
S	1.435 ± 0.289	1.158 ± 0.064
Se	ND	ND
Zn	15.866 ± 0.622	11.535 ± 0.237

ND: Not-Detected.

It should be noted that the ash fractions of tire crumbs and tire chips from dry ashing were determined as 6.64 ± 0.66 and 20.94 ± 2.89%, respectively (Table C.3). This difference was due to presence of metal wires in tire chips, as indicated with the iron measurements. In addition, experimental observations showed that the digested tire crumb solution were metallic silver in color, while the digested tire chips had bright yellow to orange color.

Some of the constituents measured in the ash content were consistent with the manufacturing information summarized in the previous chapter reported by Cummings [1998] and RMA [1998]. The presence of Al, Ca, Mg, S, and Zn is related to the rubbery portion of tire, while Fe and Cu are found in the wires inside the tires [Cummings, 1998;

RMA, 1998]. Besides these components, Cd, Cr, Mn, and Ni are considered to be present in the wires as well, although not specified in the manufacturing process. Surprisingly, small amount of Pb was detectable in all samples, even though it is not listed in the components of tires. There was no indication for the source of some other elements (e.g., Cd, Na and P). It is suspected that these compounds were mostly due to the impurities in the several chemicals used during tire manufacturing.

Laboratory Leaching Tests

Experimental matrix summarized in Table 3.1 was performed as described in the previous chapter to examine leaching of organic and inorganic constituents from scrap tires. During the leaching experiments, the following parameters were monitored: pH (adjusted back to initial leaching solutions pH after recording the daily value), DOC, DN, UV_{254} and selected inorganic constituents (S, Zn, Cd, Cr, Fe, Ca, Mg, Al, Na, P, K, As, Cu, Pb, Se, Mo, Mn, and Ni). The results will be presented in two sections: organics and inorganics. DOC and UV_{254} data were used to monitor the leaching behaviors of all organics from tires. DN was also included in the same section since this parameter is measured simultaneously with DOC, and it is related to some extent to organics since nitrogen may be present in the structure of some organic compounds. After the organic section, the results for inorganic constituents will be discussed.

Before starting to discuss the leaching behavior of organics and inorganics, the trends for the changes in pH of leaching water without any buffer will be discussed.

During the experiments, pH was monitored daily and adjusted back to the original values after the measurements using high purity 0.25 M HCl or NaOH.

Analysis of the pH data showed that scrap tires tended to drive the pH to neutral values in all cases and the highest daily changes in pH were observed within the first week. These changes decreased after each soaking cycle. An example pH fluctuation trend is shown in Figure 5.1.

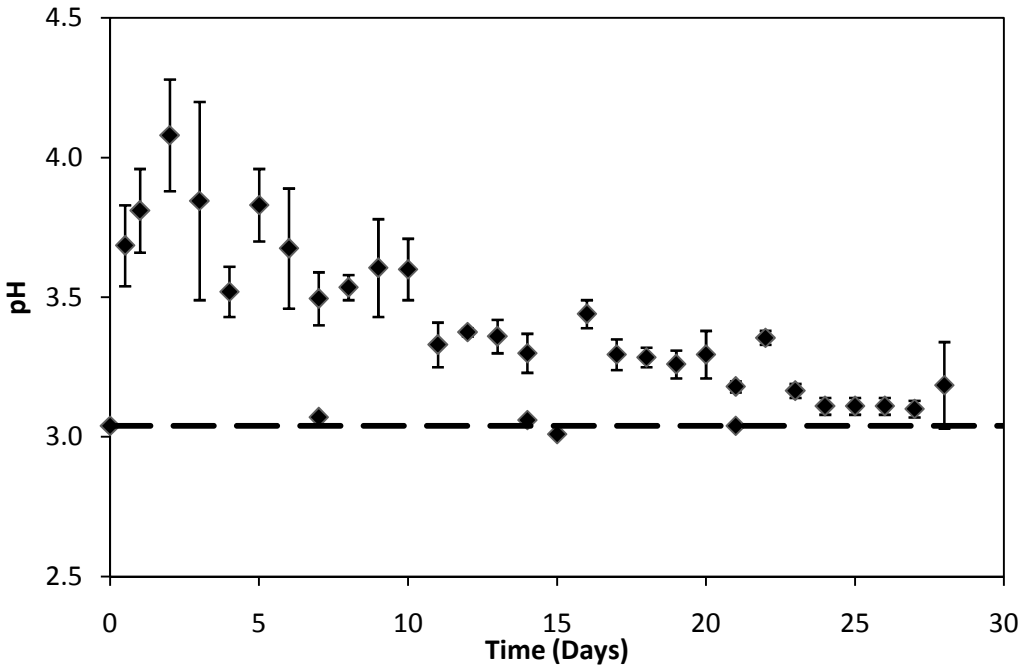


Figure 5.1: Typical pH trend (e.g. chip size 1"×1" in rainwater solution) (D.17)

Under acidic conditions, tires appeared to drive the pH to neutral conditions. This finding was consistent with Lerner et al. [1993] (Batch experiments) and Sengupta and Miller [1999] (Batch and column leaching experiments). Lerner et al. [1993] also

reported that under neutral pH conditions tires shifted the pH towards alkaline conditions. However, in this study, during pH 10.0 experiments, pH was observed to decrease. This was attributed to a combination of two factors: (i) carbon dioxide in the headspace of the reactors dissolving in water, and (ii) dissolution of iron from tires, to be discussed later in the inorganic leach

Leaching of Dissolved Organics from Scrap Tires

Due to voluminous data collected in this study, the data was compiled and presented in Appendix D. Table 5.4 shows the legend for the organic data presented in the Appendix. In this section, key findings from these results will be summarized. It should be noted in this study, leaching of nonvolatile dissolved organic compounds (i.e., DOC) were measured, showing the amount of dissolved organics that will be introduced to water sources as a result of leaching from tires. As indicated in the literature, there are some VOCs and SVOCs that have been shown to leach from tires. Since experiments were conducted in bottles with headspace and bottles were opened and closed for pH adjustment on a daily basis, the DOC values are not expected to include VOCs and SVOCs that may leach from tires. At the same time, some colloidal or small black particles were also observed during the leaching experiments; therefore although not quantified some particulate organic matter may also leach from the tires.

Table 5.4: Table numbers for matrixes presented in Appendix D

Leaching Solutions	Tire Chips				
	Crumb	1"×1"	2"×2"	4"×2"	6"×2"
pH 4.0*	D.1	D.2	D.3	D.4	D.5
pH 7.0*	D.6	D.7	D.8	D.9	D.10
pH 10.0*	D.11	D.12	D.13	D.14	D.15
Rainwater (pH: 3.0)	D.16	D.17	D.18	D.19	D.20
Soft GW (pH: 6.3)	D.21	D.22	D.23	D.24	D.25
Hard GW (pH: 8.1)	D.26	D.27	D.28	D.29	D.30

*: pH of DDW was adjusted by high purity HCl or NaOH.

Overall trend was a significant amount of DOC leaching from the scrap tires during the first week of experiments, which significantly slowed down with the renewal of leaching solution. This was consistent with the observations by O'Shaughnessy and Garga [2000]. The decrease in leaching with time is probably due to fact that the leaching occurs from the external surfaces of tires, and the easily leachable compounds are initially washed off from these surfaces at the beginning of the experiments. Then it becomes more difficult to further remove compounds from the tire surfaces with time, as water will be unable to penetrate in the non-porous tire structure [Abernethy et al., 1996].

For an easier comparison among different tire sizes and leaching solutions, the cumulative mass leaching from tires were calculated (Figure 5.2), and the overall mass leached at four week leaching period was used in the data analysis. Initially, the data obtained at different aqueous chemistry conditions will be presented in tabular (Tables 5.5 to 5.10) and in graphical format (Figures 5.3 to 5.8), then a discussion of the trends will be provided.

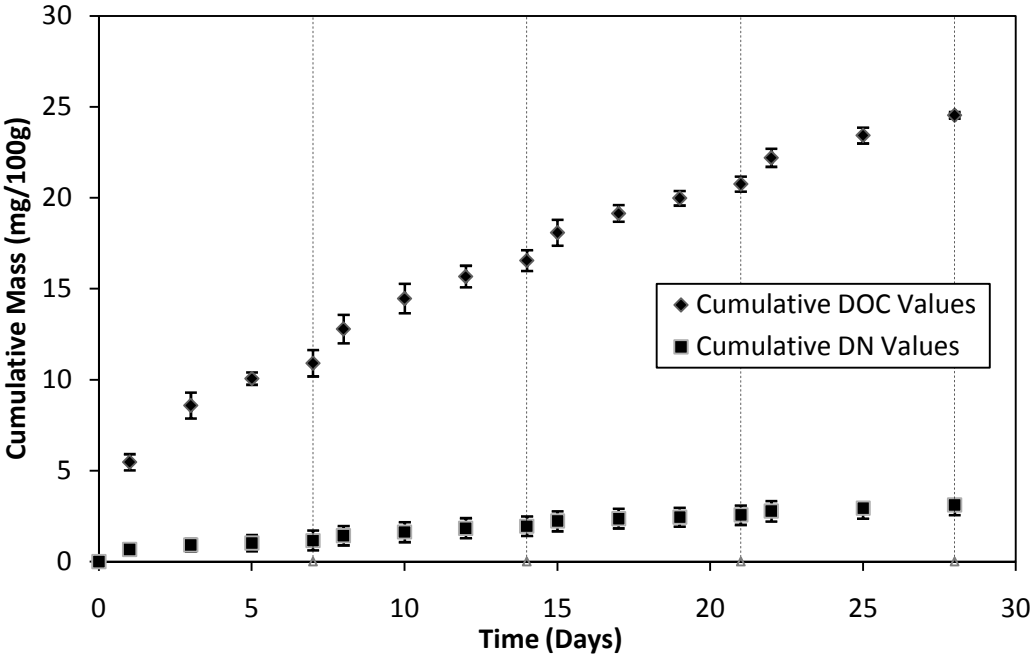


Figure 5.2: An example cumulative plot of DOC and DN leaching trend (e.g., chip size 1"×1" in rainwater solution) (D.17)

Table 5.5: Total DOC and DN mass leached from tires after 28 days in pH 4.0 solution

Tire Size	Appendix Number*	DOC (mg/100g)			DN (mg/100g)		
		Reactor 1	Reactor 2	Average DOC	Reactor 1	Reactor 2	Average DN
Crumb	D.1	42.82	44.31	43.56	5.48	5.76	5.62
1"×1"	D.2	18.97	19.89	19.43	3.26	2.70	2.98
2"×2"	D.3	12.61	12.68	12.65	1.75	1.85	1.80
4"×2"	D.4	8.65	9.77	9.21	1.48	1.26	1.37
6"×2"	D.5	8.13	10.70	9.41	1.19	1.47	1.33

*: Table # in the Appendix where the data provided in this table can be found as a function of time.

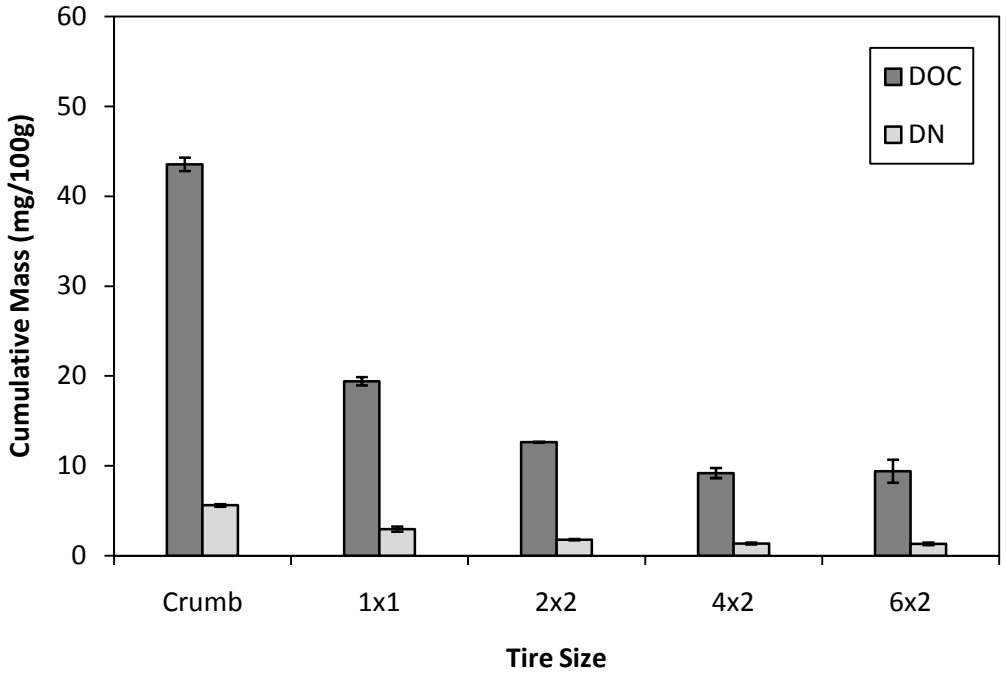


Figure 5.3: Total DOC and DN mass leached from tires after 28 days in pH 4.0 solution

Table 5.6: Total DOC and DN mass leached from tires after 28 days in pH 7.0 solution

Tire Size	Appendix Number*	DOC (mg/100g)				DN (mg/100g)			
		React. 1	React. 2	React. 3	Ave. DOC	React. 1	React. 2	React. 3	Ave. DN
Crumb	D.6	55.04	57.59		56.32	5.75	6.01		5.88
1"×1"	D.7	17.50	19.95	21.22	19.56	2.59	3.20	3.09	2.96
2"×2"	D.8	14.49	11.43		12.96	1.26	1.20		1.23
4"×2"	D.9	11.23	10.62		10.92	2.41	2.96		2.68
6"×2"	D.10	13.79	9.96		11.88	1.99	1.29		1.64

*: Table # in the Appendix where the data provided in this table can be found as a function of time.

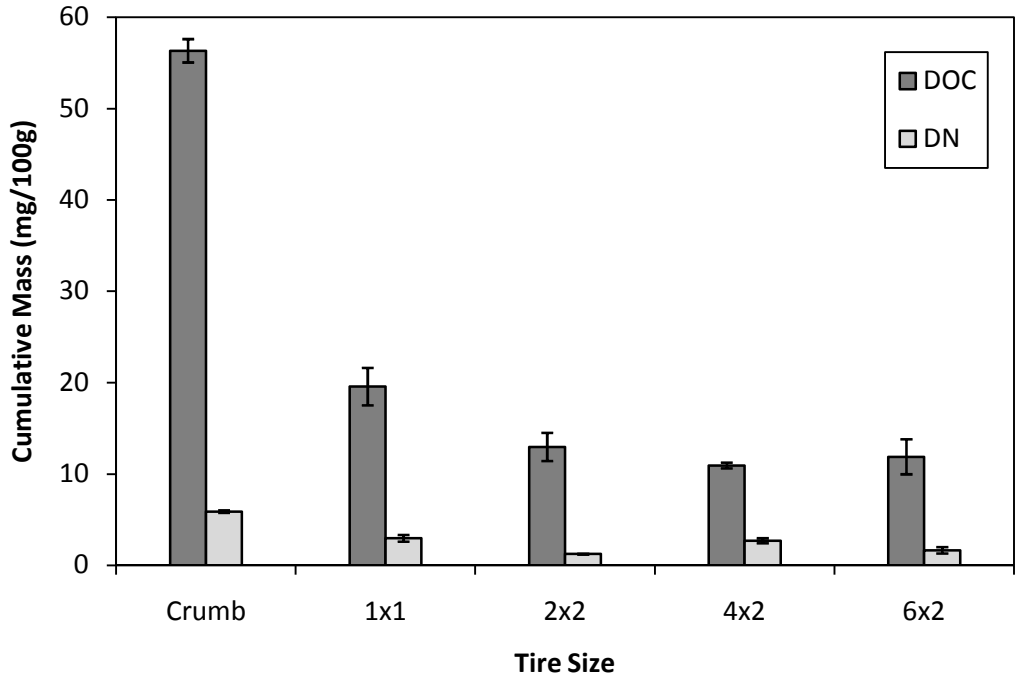


Figure 5.4: Total DOC and DN mass leached from tires after 28 days in pH 7.0 solution

Table 5.7: Total DOC and DN mass leached from tires after 28 days in pH 10.0 solution

Tire Size	Appendix Number*	DOC (mg/100g)				DN (mg/100g)			
		React. 1	React. 2	React. 3	Ave. DOC	React. 1	React. 2	React. 3	Ave. DN
Crumb	D.11	118.39	126.17		122.28	5.02	5.21		5.12
1"×1"	D.12	27.04	27.02		27.03	2.47	2.88		2.67
2"×2"	D.13	26.53	28.10		27.31	2.17	1.78		1.97
4"×2"	D.14	23.40	28.58	17.25	23.08	2.84	3.14	1.67	2.55
6"×2"	D.15	14.62	22.75		18.68	1.24	1.67		1.45

*: Table # in the Appendix where the data provided in this table can be found as a function of time.

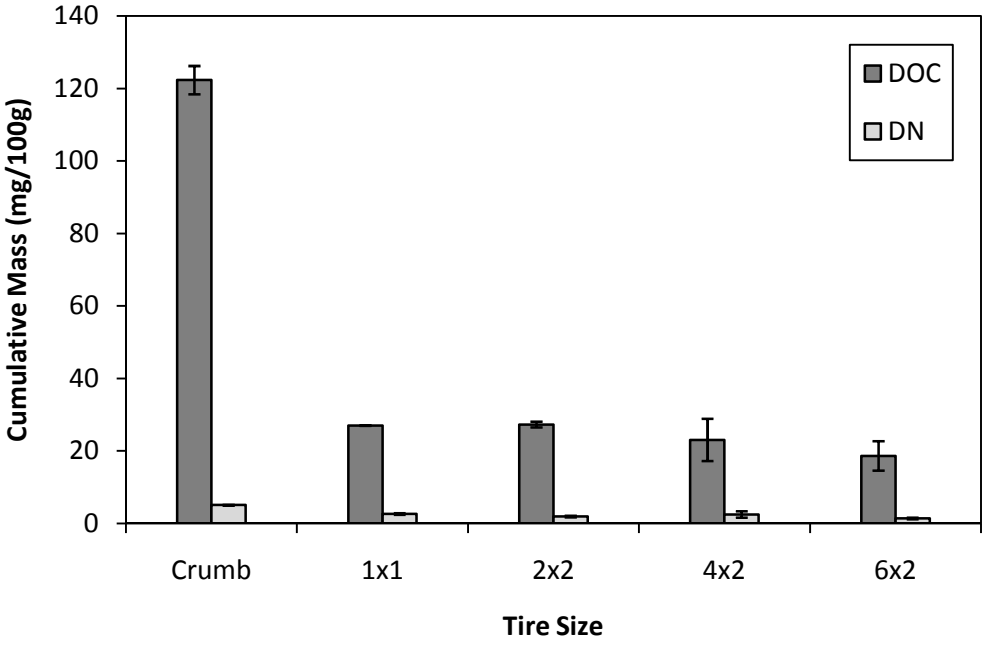


Figure 5.5: Total DOC and DN mass leached from tires after 28 days in pH 10.0 solution

Table 5.8: Total DOC and DN mass leached from tires after 28 days in rainwater at pH 3.0

Tire Size	Appendix Number*	DOC (mg/100g)			DN (mg/100g)		
		Reactor 1	Reactor 2	Average DOC	Reactor 1	Reactor 2	Average DN
Crumb	D.16	60.14	64.72	62.43	7.73	8.60	8.17
1"×1"	D.17	24.37	24.73	24.55	2.56	3.67	3.12
2"×2"	D.18	15.19	13.55	14.37	1.97	1.96	1.96
4"×2"	D.19	9.51	14.05	11.78	1.41	2.11	1.76
6"×2"	D.20	12.72	12.49	12.61	1.46	1.72	1.59

*: Table # in the Appendix where the data provided in this table can be found as a function of time.

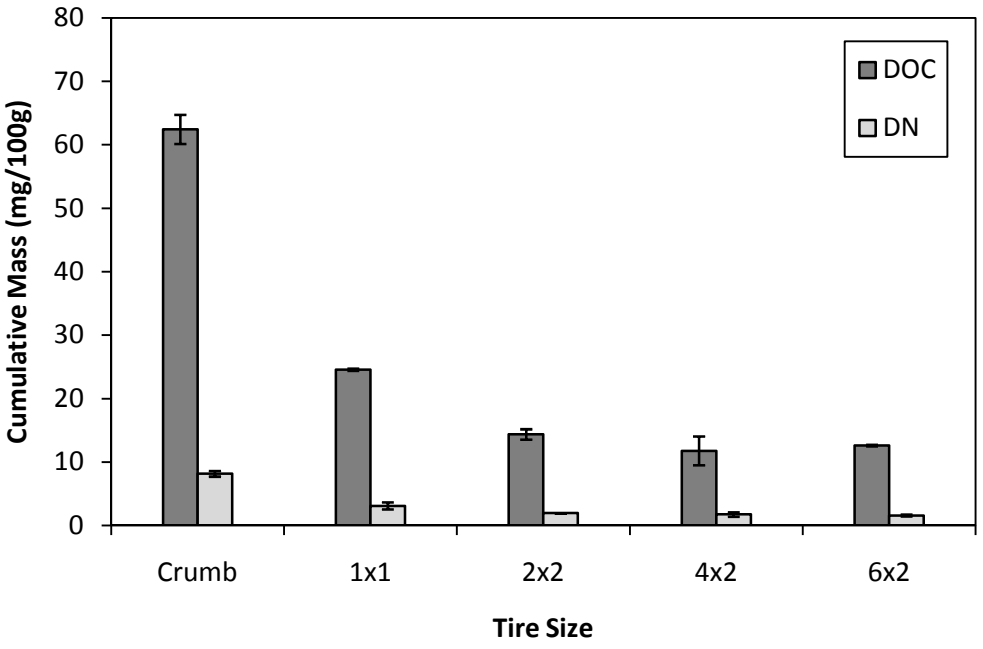


Figure 5.6: Total DOC and DN mass leached from tires after 28 days in rainwater at pH 3.0

Table 5.9: Total DOC and DN mass leached from tires after 28 days in soft groundwater at pH 6.3

Tire Size	Appendix Number*	DOC (mg/100g)			DN (mg/100g)		
		Reactor 1	Reactor 2	Average DOC	Reactor 1	Reactor 2	Average DN
Crumb	D.21	47.53	50.89	49.21	5.58	6.07	5.83
1"×1"	D.22	15.23	20.66	17.95	1.90	2.96	2.43
2"×2"	D.23	9.61	12.13	10.87	1.18	1.31	1.24
4"×2"	D.24	16.94	16.25	16.59	1.94	1.20	1.57
6"×2"	D.25	14.55	17.21	15.88	1.24	2.66	1.95

*: Table # in the Appendix where the data provided in this table can be found as a function of time.

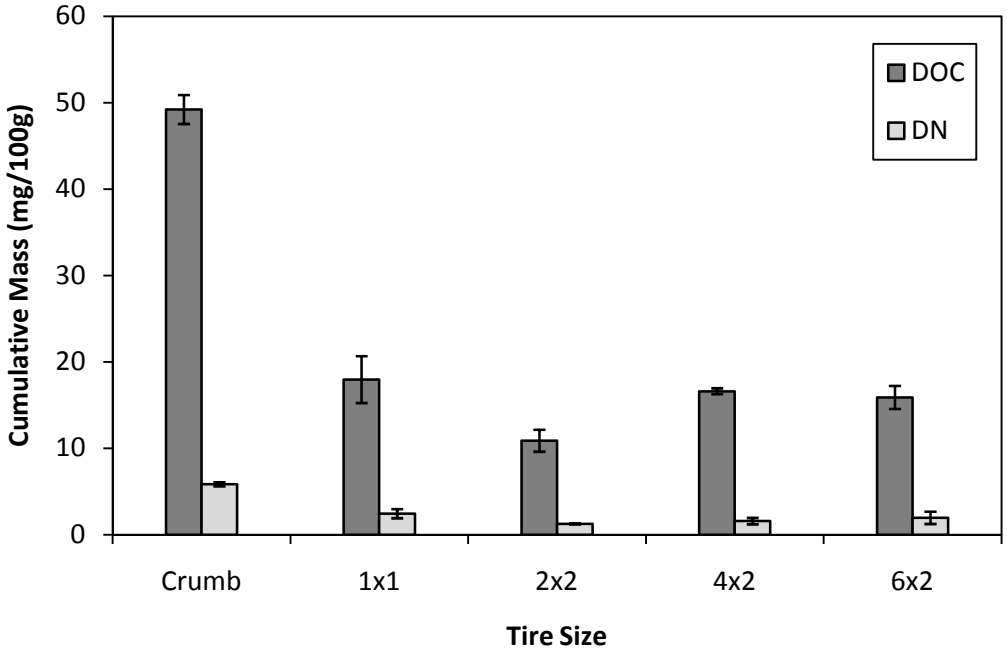


Figure 5.7: Total DOC and DN mass leached from tires after 28 days in soft groundwater at pH 6.3

Table 5.10: Total DOC and DN mass leached from tires after 28 days in hard groundwater at pH 8.1

Tire Size	Appendix Number*	DOC (mg/100g)			DN (mg/100g)		
		Reactor 1	Reactor 2	Average DOC	Reactor 1	Reactor 2	Average DN
Crumb	D.26	60.00	62.50	61.25	4.88	4.96	4.92
1"×1"	D.27	22.56	17.81	20.19	2.86	2.30	2.58
2"×2"	D.28	16.21	21.37	18.79	1.05	1.32	1.19
4"×2"	D.29	9.63	12.04	10.84	1.14	1.07	1.10
6"×2"	D.30	14.57	14.62	14.60	1.94	1.37	1.66

*: Table # in the Appendix where the data provided in this table can be found as a function of time.

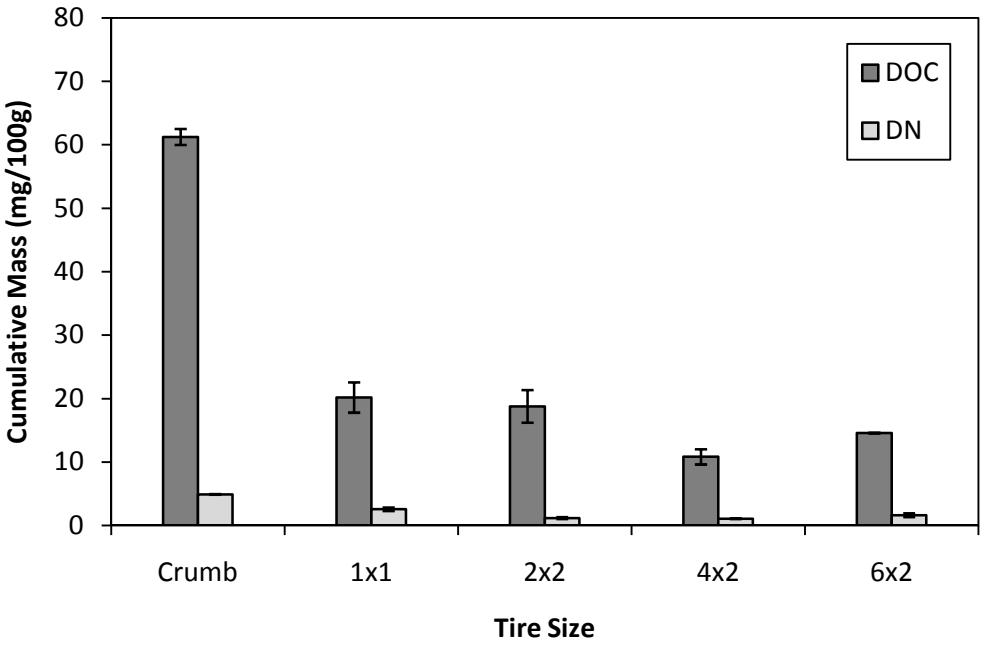


Figure 5.8: Total DOC and DN mass leached from tires after 28 days in hard groundwater at pH 8.1

The Effect of Chip Size on Leaching

The results show that there is a size effect on the leaching of both DOC and DN in all six leaching solutions. As expected, crumb tires showed significantly higher amount of leaching than tire chips due to their larger surface area (resulting from their very small sizes) than tire chips. As for the tire chips, the smallest size chips (1"×1") showed the highest degree of leaching, while the leaching from chips 2"×2", 4"×2" and 6"×2" were relatively comparable with each other. To examine the influence of tire surface area on leaching, DOC masses leached were normalized for tire chips using the calculated total surface area from Table 4.1. The total surface normalized values still showed higher degree of leaching from 1"×1" particles than the other particle sizes (Table 5.11). Since total top and bottom surface areas of tire chips among all sizes were comparable (Table 4.1), it was hypothesized that one possibility for the difference observed in organics leaching may be related to the amount of side surfaces of the tire chips. The top and bottom surfaces of the tires have been probably weathered during the use and/or storage. Therefore, higher and fast organic leaching probably occurred from the sides that were freshly opened when the tires were cut to prepare the chips. When the leaching data was normalized based on calculated side-surface areas of the tire chips, the leaching results appeared to be less dependent of particle size (Table 5.11). This analysis suggested that fresh surface areas of tire chips, especially the area that became available fresh, was an important factor controlling the total mass of DOC leaching from scrap tires. On the other hand, when the leaching on a surface area basis was compared between tire chips and crumb rubber (using either BET surface area or the calculated values in Table 4.1), it was

surprisingly observed that leaching from crumb rubber (0.01 mg/inch^2 (based on the calculated surface area), and 0.4×10^{-3} mg/inch^2 (based on the measured surface area)) was significantly lower than leaching tire chips (ranging from 0.2 to 0.6 mg/inch^2). This was unexpected because crumb rubber had significant amount of fresh surfaces exposed to the solutions. One possibility may be the impact of pulverization processes during crumb rubber preparation. However, this was not further investigated in this study, since the main focus was on the leaching from tire chips.

Considering SC standards regarding reuse of scrap tires (i.e., tire chips must be between 0.5 and 4 inches in size with steel wires not protruding more than 0.5 inch from the sides of the chips), these experiments showed that when scrap tire chips are employed at sizes 2"×2", 4"×2" and 6"×2", the effect of particle size on the total amount of DOC leaching will be small for the same mass of tire chips. However, higher degree of DOC leaching will increase if 1"×1" or smaller size tire chips, especially crumb tires, are employed.

Table 5.11: Total DOC mass and surface area-normalized DOC mass leached from tire chips

Leaching Solution/Tire Size[a]		Total DOC Mass Leached (mg)	Ratio 1[b]	DOC/Total Surface Area (mg/inch^2)	Ratio 2[c]	DOC/Side Surface Area (mg/inch^2)	Ratio 3[d]
Rain water (pH 3.0)	1"×1"	24.55	1.00	0.51	1.00	1.53	1.00
	2"×2"	14.37	0.59	0.32	0.63	1.12	0.73
	4"×2"	11.78	0.48	0.28	0.55	1.23	0.80
	6"×2"	12.61	0.51	0.41	0.81	1.97	1.28
pH 4.0*	1"×1"	19.43	1.00	0.40	1.00	1.21	1.00
	2"×2"	12.65	0.65	0.28	0.70	0.99	0.81
	4"×2"	9.21	0.47	0.22	0.55	0.96	0.79
	6"×2"	9.41	0.48	0.31	0.77	1.47	1.21
Soft GW (pH 6.3)	1"×1"	17.95	1.00	0.37	1.00	1.12	1.00
	2"×2"	10.87	0.61	0.24	0.65	0.85	0.76
	4"×2"	16.59	0.92	0.40	1.07	1.73	1.54
	6"×2"	15.88	0.88	0.52	1.40	2.48	2.21
pH 7.0*	1"×1"	19.56	1.00	0.41	1.00	1.22	1.00
	2"×2"	12.96	0.66	0.29	0.71	1.01	0.83
	4"×2"	10.92	0.56	0.26	0.64	1.14	0.93
	6"×2"	11.88	0.61	0.39	0.96	1.86	1.52
Hard GW (pH 8.1)	1"×1"	20.19	1.00	0.42	1.00	1.26	1.00
	2"×2"	18.79	0.93	0.42	1.00	1.47	1.16
	4"×2"	10.84	0.54	0.26	0.62	1.13	0.89
	6"×2"	14.60	0.72	0.48	1.14	2.28	1.81
pH 10.0*	1"×1"	27.03	1.00	0.56	1.00	1.69	1.00
	2"×2"	27.31	1.01	0.61	1.08	2.13	1.26
	4"×2"	23.08	0.85	0.55	0.99	2.40	1.42
	6"×2"	18.68	0.69	0.61	1.09	2.92	1.73

*: pH of DDW was adjusted by high purity HCl or NaOH.

[a] : Crumb rubber is not included in the table since it was not possible to estimate its total surface area in a bottle.

[b] : The ratio of DOC mass leached from different tire sizes to DOC mass leached from 1"×1" tires in each solution.

[c] : The ratio of DOC/Total Surface Area from different tire sizes to DOC/Total Surface Area from 1"×1" tires in each solution.

[d] : The ratio of DOC/Side Surface Area from different tire sizes to DOC/Side Surface Area from 1"×1" tires in each solution.

The Effects of pH and Conductivity on DOC Leaching:

Initially, the results for the three leaching solutions at different pH values (4.0, 7.0, and 10.0) were compared in order to examine the pH effect. The trend was consistent with that was reported by Twin City Testing Corporation [1990]. It was observed that there was a higher degree of DOC leaching at basic conditions than neutral and acidic pH conditions (Figure 5.9). The trend was same for all tire chip sizes (Table 5.12). On the other hand, no pH impact was observed the leaching of DN.

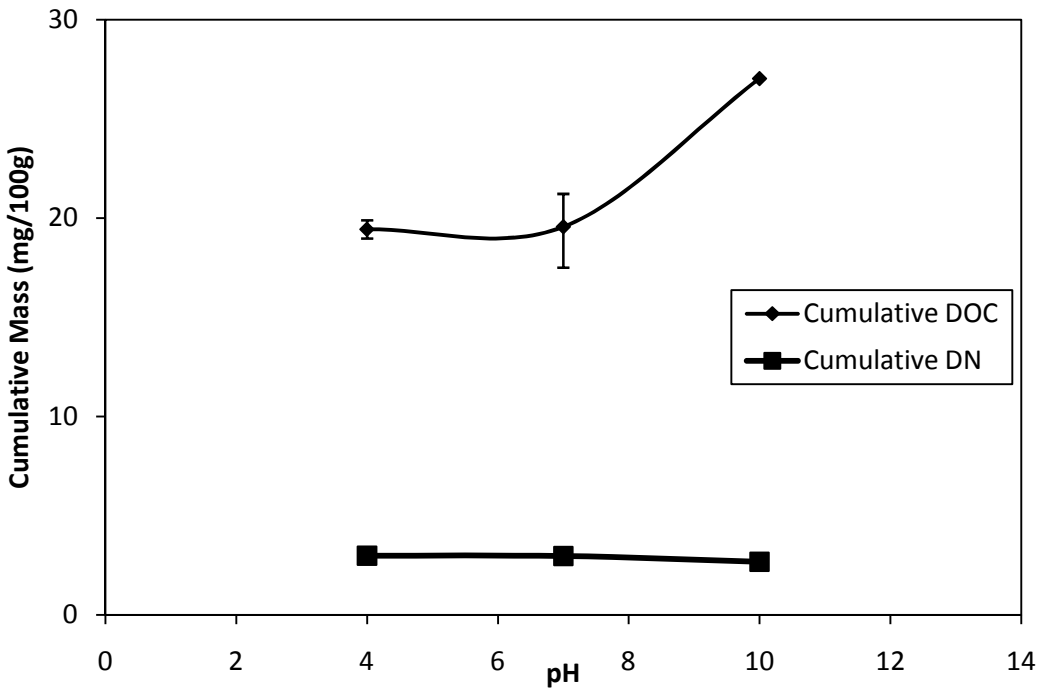


Figure 5.9: DOC leaching for leaching solutions at pH 4.0, 7.0 and 10.0 (Chip size 1"×1")

Table 5.12: DOC leaching in solutions at pH 4.0, 7.0 and 10.0

Leaching Solutions	Tire Chips				
	Crumb	1"×1"	2"×2"	4"×2"	6"×2"
pH 4.0*	43.56	19.43	12.65	10.51	9.41
pH 7.0*	56.32	19.56	12.96	10.92	11.88
pH 10.0*	122.28	27.03	27.31	23.08	18.68

*: pH of DDW was adjusted by high purity HCl or NaOH.

When the groundwater solutions, having higher conductivity values, were also included in the comparison (Figure 5.10 and Table 5.13), in general, there was no major changes in the observed trend. However, a few exceptions have been noted such as hard ground water conditions for size 1"×1" and soft groundwater for size 4"×2". Usually more variability in the trends for chip size of 6"×2" was observed during the experiments. One reason for this observation is probably the fact that a single chip was used in each bottle during the leaching experiments (Table 4.1). Although maximum attention was placed to selecting tire chips as uniform as possible with similar shapes and sizes, there were higher possibility for variability in the 6"×2" chip experiments than smaller chip size experiments with higher number of chips in the leaching solution. The results from these experiments indicated that changes in background conductivity did not have a significant impact on the leaching of the organics. This was also consistent with the findings of Lerner et al. [1993] that change in conductivity of solution has little to no impact on the leaching.

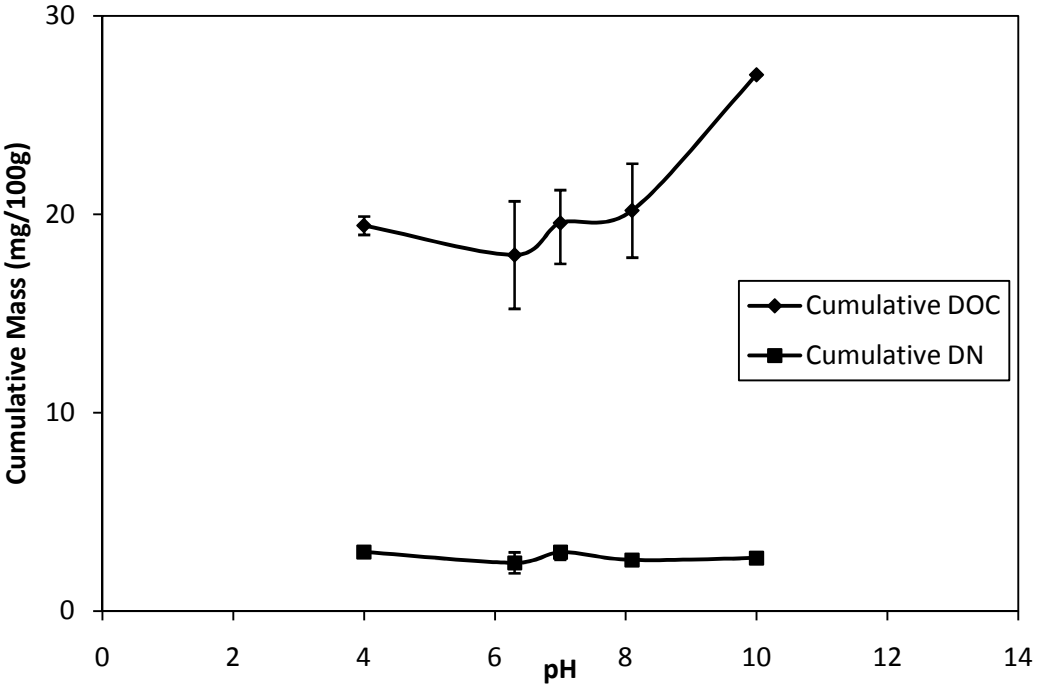


Figure 5.10: DOC leaching for leaching solutions at pH 4.0, 7.0 and 10.0 and groundwater solutions (Chip size 1"×1")

As the results indicated that conductivity did not have a significant impact on the leaching, the data from all the experiments were compared together. The Table 5.13 and Figure 5.11 show the overall results.

Table 5.13: Total DOC mass leached under different aqueous chemistry conditions (mg)

Leaching Solutions	Tire Chips				
	Crumb	1"×1"	2"×2"	4"×2"	6"×2"
Rainwater (pH: 3.0)	62.43	24.55	14.37	11.78	12.61
pH 4.0*	43.56	19.43	12.65	10.51	9.41
Soft GW (pH: 6.3)	49.21	17.95	10.87	16.59	15.88
pH 7.0*	56.32	19.56	12.96	10.92	11.88
Hard GW (pH: 8.1)	61.25	20.19	18.79	10.84	14.60
pH 10.0*	122.28	27.03	27.31	23.08	18.68

*: pH of DDW was adjusted by high purity HCl or NaOH.

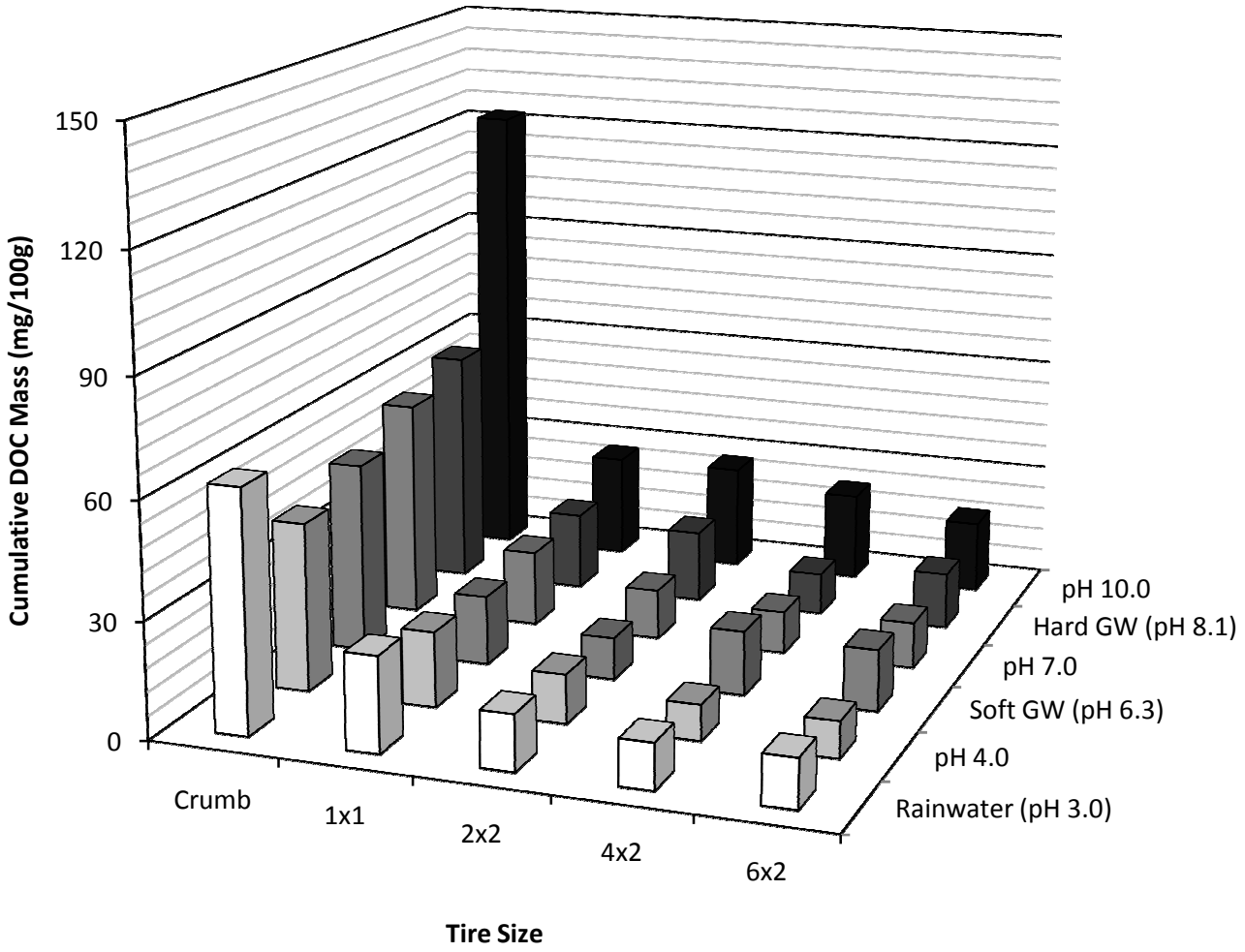


Figure 5.11: DOC leaching from scrap tires at all conditions tested during this study

When the results for the rainwater leaching data were compared with the rest of the experiments, it was noted that the leaching in the rainwater was usually higher than other conditions tested, except the basic conditions (i.e., leaching solution at pH 10.0). The trends indicated that basic conditions significantly enhance leaching of DOC from scrap tires. Some increase in the amount of DOC leaching was observed under the lowest pH condition (pH 3.0) tested. The lowest DOC leaching occurred in the pH range of 4 to 8. This leaching behavior can be explained with two different mechanisms. Dissolution of PAHs and TPHs under basic conditions increases as reported in the Twin City Testing Corporation [1990] study. On the other hand, under acidic conditions the physical structure of tire can be disrupted resulting in leaching of more organic compounds. During the experiments, some black residues were accumulated on the sample filtering discs for acidic samples (Rainwater at pH 3.0 and leaching solution at pH 4.0).

Overall, these experimental results demonstrated that leaching of DOC from scrap tires will be minimum when tires are exposed to pH conditions around neutral values. This is not surprising because tires are design to perform the best and to deteriorate the list under such conditions. Therefore, using tires under similar conditions during reuse applications will minimize leaching of DOC from tires. On the other hand, the highest DOC leaching will occur at the high pH values. Therefore, such conditions should be avoided to minimize the leaching of organics. The results also showed that pH is a more important factor controlling the leaching of DOC from tires. No significant impact of conductivity has been observed for DOC leaching.

The overall trend for the leaching of DN was summarized in Table 5.14 and plotted in Figure 5.12. The effect of pH on the DN leaching was less apparent. It should be noted that there is no apparent source of nitrogen in tire manufacturing processes, and nitrogen only constituted 0.43% weight of total weight measured in crumb tire in this study (Table 5.1). No additional measurements were conducted to further characterize the nature of nitrogen (NO_3^-, NO_2^-, NH_3 and organic nitrogen) leaching from tires. There may be some nitrogenous organic compounds in the tires; leaching of benzothiazole, aniline and benzothiazolone from tires have been reported [Spagnoli et al., 2001; O'Shaughnessy and Garga, 2000; Azizian and Nelson, 2003].

Table 5.14: Total DN mass leached under different aqueous chemistry conditions (mg)

Leaching Solutions	Tire Chips				
	Crumb	1"×1"	2"×2"	4"×2"	6"×2"
Rainwater (pH: 3.0)	8.17	3.12	1.96	1.76	1.59
pH 4.0*	5.62	3.81	1.80	1.79	1.33
Soft GW (pH: 6.3)	5.83	2.43	1.24	1.57	1.95
pH 7.0*	5.88	2.96	1.23	2.68	1.64
Hard GW (pH: 8.1)	4.92	2.58	1.19	1.10	1.66
pH 10.0*	5.12	3.68	1.97	2.55	1.45

*: pH of DDW was adjusted by high purity HCl or NaOH.

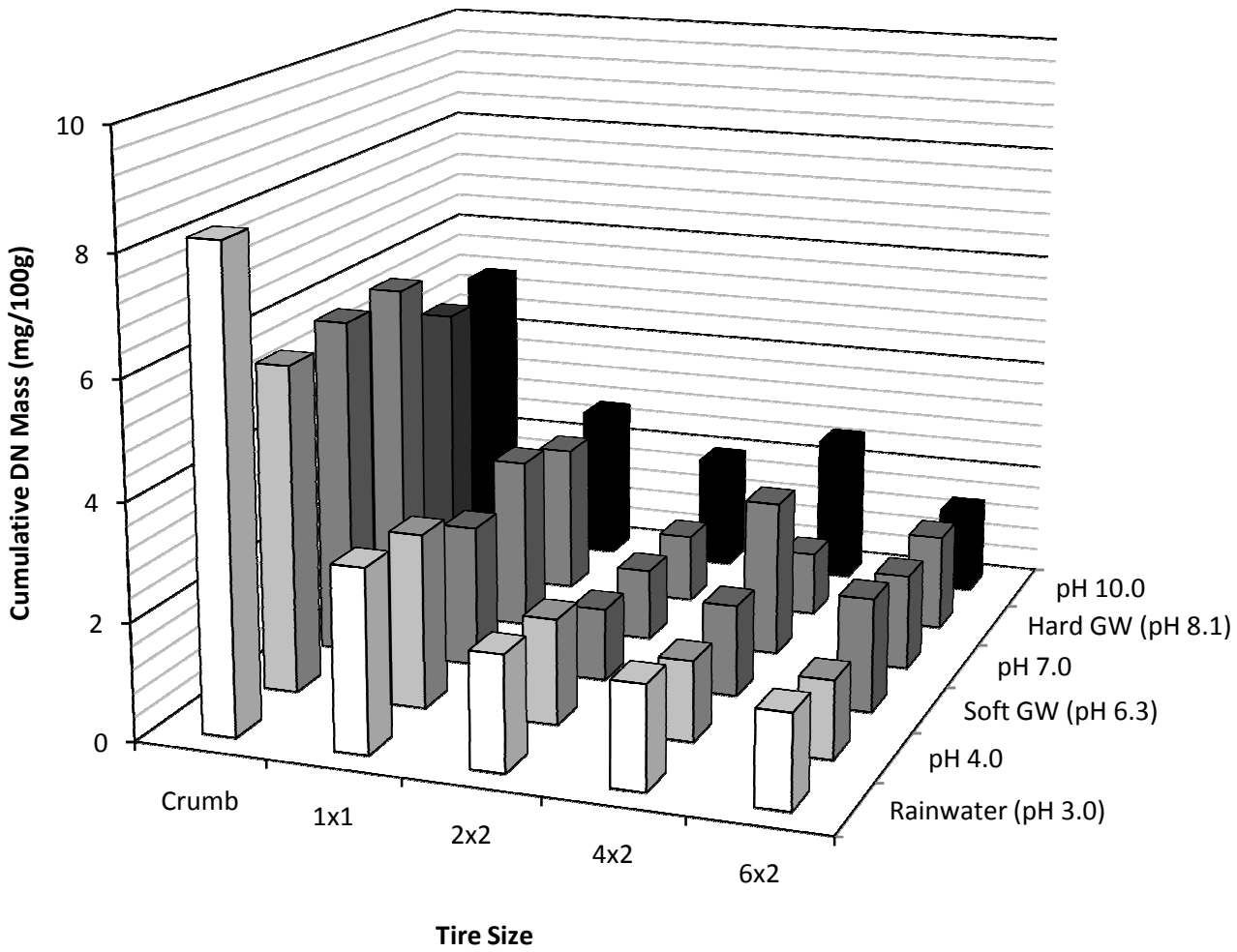


Figure 5.12: DN leaching from scrap tires at all conditions tested during this study

$SUVA_{254}$:

In order to gain some insight to the characteristics of organic compounds leaching from tires, $SUVA_{254}$ values were also determined. $SUVA_{254}$ is the ratio of Ultraviolet absorbance at 254 nm wavelength (UV_{254}) to DOC in a sample, and it is used as an indication of the aromatic organic carbon content in a sample [Karanfil et al., 2002]. Initial (i.e., the value at the end of the first week during leaching) and final (i.e., the value at the end of the fourth week during leaching) $SUVA_{254}$ values measured during the experiments are provided in Table 5.15.

Table 5.15: $SUVA_{254}$ (L/mg-m) values (Initial→Final)

Leaching Solutions	Tire Chips				
	Crumb	1"×1"	2"×2"	4"×2"	6"×2"
Rainwater (pH: 3.0)	1.5 → 1.5	3.5 → 5.5	5.5 → 10.0	7.0 → 12.0	5.0 → 10.0
pH 4.0*	2.0 → 3.0	2.5 → 3.0	2.0 → 3.0	3.0 → 5.0	3.5 → 6.5
Soft GW (pH: 6.3)	1.5 → 2.0	2.0 → 3.0	2.0 → 2.0	2.0 → 3.0	1.5 → 2.0
pH 7.0*	1.5 → 2.0	2.0 → 2.5	3.5 → 3.5	2.5 → 3.0	3.0 → 3.5
Hard GW (pH: 8.1)	1.5 → 2.0	2.0 → 2.5	2.0 → 2.0	2.5 → 2.5	2.5 → 2.0
pH 10.0*	1.5 → 1.5	2.0 → 3.0	2.0 → 1.5	2.5 → 2.0	2.0 → 1.5

*: pH of DDW was adjusted by high purity HCl or NaOH.

The results indicated that the $SUVA_{254}$ values of the leaching solutions remained in the range of 1.5 to 3.0 L/mg-m during the experiments, except for rainwater samples. There was a gradual increase in the $SUVA_{254}$ values after the first week, indicating an increase in the fraction of aromatic carbons leaching from the tires over time. This increase was no more than one unit, except rainwater samples. This trend suggested that some non-aromatic (e.g., aliphatic) compounds were dissolved quickly at the beginning

of the leaching experiments, which was followed by dissolution of more aromatic components with time.

The only exception observed was for the rainwater samples, in which the initial $SUVA_{254}$ values were recorded at 5.0 and increased up to 12.0 L/mg-m with time. In order to minimize the potential measurement interference on the result that may arise from the low pH of rainwater samples (pH 3.0), the pH of selected samples were adjusted to pH 7.0 and measured again. The comparison of the original and pH-adjusted samples showed no significant difference on the UV_{254} measurements. Therefore, high $SUVA_{254}$ values observed in the rainwater was attributed to the very low pH values of rainwater (pH 3.0) on the tires. During these experiments, some amount black particulate matter was accumulated on the filter discs. This was attributed to the deterioration of the integrity of tires under acidic conditions.

Identification of Organic Compounds:

In order to gain some insight to the type of organic compounds leaching from scrap tires, crumb tires leachates from experiments at pH 4.0, 7.0 and 10.0 after one week of leaching period were extracted with MTBE and scanned with a GC/MS/MS system. As discussed before, the conditions for the scans and extractions were not optimized and the goal was to obtain some qualitative insight to the types of organics in the leachate. As a result, the concentrations of the detected organics were not quantified. An example chromatogram from these scans is shown in Figure 5.13.

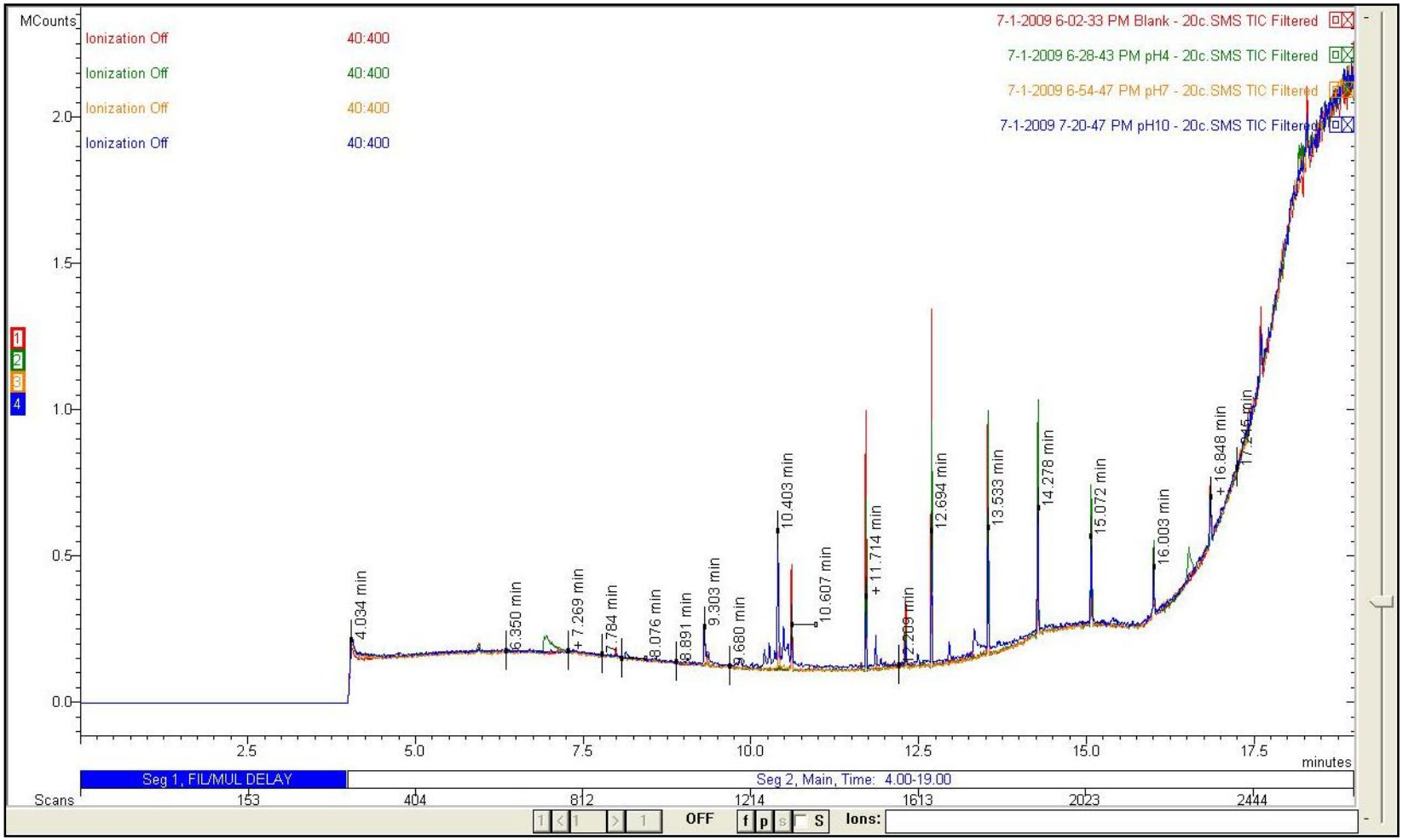


Figure 5.13: Chromatogram of organics analysis

The peaks were analyzed with the library provided by the software of the instrument. The list of identified organics is given in Table 5.16.

Table 5.16: List of identified organics in leachates from tires

Organic Compound	Molecular Formula	pH 4.0*	pH 7.0*	pH 10.0*
Dimethyl Sulfoxide	C_2H_6OS	✓	ND	✓
Aniline	C_6H_7N	ND	ND	✓
2,5-CycloHexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)-	$C_{14}H_{20}O_2$	ND	ND	✓
Hexanoic Acid, 2-ethyl-	$C_8H_{16}O_2$	ND	ND	✓
Neodecanoic Acid	$C_{10}H_{20}O_2$	ND	ND	✓
Benzothiazole	C_7H_5NS	✓	✓	✓
Benzothiazolone	C_7H_5NOS	ND	ND	✓
2,3-Di-O-methyl-D-xylopyranose	$C_7H_{14}NO_5$	ND	✓	✓
Benzothiazole, 2-(methylthio)-	$C_8H_7NS_2$	ND	ND	✓
Thiophene, tetrohydro-2methyl-	$C_5H_{10}S$	ND	ND	✓
4'-Ethoxy-2'hydroxyoctadecanophenone	$C_{26}H_{44}O_3$	ND	ND	✓
Benzylamine	C_7H_9N	ND	ND	✓

*: pH of DDW was adjusted by high purity HCl or NaOH.
ND: Not Detected.

Even though the extraction method was not fully developed, organics were mostly aromatic hydrocarbons. This is consistent with the previous study by Twin City Testing Corporation's [1990]. In addition, consistent with the DOC leaching trends and the Twin City Testing Corporation's [1990] study, the sizes and number of the peaks at pH 10.0 leachates were relatively higher as compared to other pH conditions.

Due to structure of tires and the experimental methods employed in this study, the samples were not expected to have volatile organics in them. Most of the organics that were determined during the GC/MS/MS scan have a boiling point of 200^{o}C or above.

One of the concerns with the leaching of some of these organic compounds is their potential health effects. The current knowledge on these compounds indicates that most of them are classified as harmful and some are classified possible carcinogens (e,g., aniline). Thus, a land application of tires may cause adverse health effects and result in a contamination of local water sources. However, only a small number of organics in the leachate were qualitatively determined during this study due to funding and time limitations. It is important to determine their concentrations especially in field studies because they can be diluted to the levels well below their detection limits reducing their environmental impact. However, the small number of scans conducted in this study document the leaching of some specific organic compounds from scrap tires. Some of these compounds (e.g., aniline, benzothiazole, benzothiazolone) have been also reported in previous studies [Spagnoli et al., 2001; O'Shaughnessy and Garga, 2000; Azizian and Nelson, 2003] along with many other compounds (e.g., Dimethyl Sulfoxide, 2,5-CycloHexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)-, Hexanoic Acid, 2-ethyl-, Neodecanoic Acid, 2,3-Di-O-methyl-D-xylopyranose, Benzothiazole, 2-(methylthio)-, Thiophene, tetrahydro-2-methyl-, 4'-Ethoxy-2'hydroxyoctadecanophenone, and benzylamine). It is likely that there are many other compounds that have not been identified so far. Therefore, there is a research need for further identification and quantification of organic compound leaching from scrap tires and assess their potential environmental impacts during various land applications.

Leaching Rate:

Analysis of cumulative leaching data reveals an interesting observation. Previously, Azizian and Nelson [2003] reported for Al, Hg and benzothiazole that 50% of leaching occurred in the first 10 hours of the one week leaching experiments. Using a similar approach, the cumulative mass at the end of four weeks were used as 100% of leaching (M_{Max}) for the data set, and for each day the ratio of cumulative DOC mass leached to total leached DOC mass were calculated (M/M_{Max}). It was found that leaching rate was almost the same for all conditions tested regardless of tire type and leaching solution (Figure 5.14). The mass of DOC leached during the first 12 hr consisted of 40-50% of the leaching during the first week and 20-25% of the leaching during the four weeks of experiments. Although the cumulative DOC mass leached from tires depended on tire size and leaching solution, the leaching rate remained constant. The leaching graph of DOC is presented in Figure 5.14.

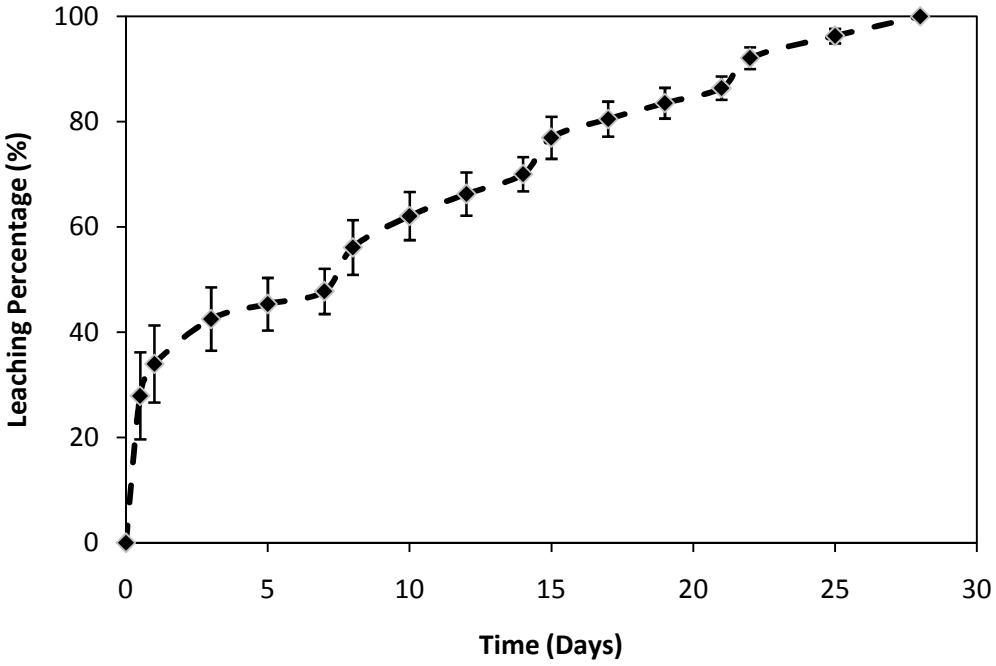


Figure 5.14: Average DOC leaching rate for experimental conditions

Leaching of Inorganics from Scrap Tires

The leachates from scrap tires were analyzed for a suite of elements that were in the analytical protocol developed for ICP analysis: S, Zn, Cd, Cr, Fe, Ca, Mg, Al, Na, P, K, As, Cu, Pb, Se, Mo, Mn, and Ni. The results showed that As, Cd, Cr, Cu, Mo, Se, Ni and Pb were below the detection limits during one month of leaching experiments. Phosphorus was detected only in few samples, thus it was not included in the data discussion. Due to daily pH adjustments using sodium hydroxide, changes in sodium was not evaluated. From the remaining elements, Al, S, Zn, Fe, Ca, Mg, Mn and K were detected in all samples and discussed in this section.

As for organics, due to the voluminous data obtained during these experiments, average daily concentrations of elements are in given in Appendix E. Table 5.17 shows the legend for the data presented in Appendix E. In this section, key findings from these results will be summarized.

Table 5.17: Table numbers for the data presented in Appendix E

Leaching Solutions	Crumb	Tire Chips			
		1"×1"	2"×2"	4"×2"	6"×2"
DDW at pH 4.0	E.1	E.2	E.3	E.4	E.5
DDW at pH 7.0	E.6	E.7	E.8	E.9	E.10
DDW at pH 10.0	E.11	E.12	E.13	E.14	E.15
Rainwater (pH: 3.0)	E.16	E.17	E.18	E.19	E.20
Soft GW (pH: 6.3)	E.21	E.22	E.23	E.24	E.25
Hard GW (pH: 8.1)	E.26	E.27	E.28	E.29	E.30

Initially, a discussion for leaching of the measurable elements was presented, then an overall comparison and evaluation of the data was provided. For Al, Zn, Fe, and Mn, the results will be discussed for all experimental conditions because these elements were not found in any freshly prepared leaching solution, as confirmed with the ICP-OES measurements of the solutions before the leaching experiments. For S, Ca, Mg, and K, since they are already found in the stimulant solutions used in this study, their leaching was only examined in leaching solutions at pH 4.0, 7.0 and 10.0.

Iron, Manganese, Zinc and Aluminum:

The cumulative masses for iron, manganese, zinc and aluminum leached during the four weeks experiments are provided in Tables 5.18 to 5.21.

Table 5.18: Total iron mass (mg) leached from tires after 28 days

Leaching Solutions	Tire Chips				
	Crumb	1"×1"	2"×2"	4"×2"	6"×2"
Rainwater (pH: 3.0)	20.02	834.47	294.37	282.57	545.64
pH 4.0*	3.52	146.41	125.92	142.90	75.98
Soft GW (pH: 6.3)	0.11	1.73	2.94	1.80	2.48
pH 7.0*	0.09	0.03	0.64	0.03	0.40
Hard GW (pH: 8.1)	0.08	0.15	0.21	0.04	0.12
pH 10.0*	0.11	0.36	0.85	0.48	0.47

*: pH of DDW was adjusted by high purity HCl or NaOH.

Table 5.19: Total manganese mass (mg) leached from tires after 28 days

Leaching Solutions	Tire Chips				
	Crumb	1"×1"	2"×2"	4"×2"	6"×2"
Rainwater (pH: 3.0)	0.87	5.52	2.17	2.58	3.49
pH 4.0*	0.74	2.61	1.73	1.69	0.77
Soft GW (pH: 6.3)	0.36	0.84	0.74	0.43	0.56
pH 7.0*	0.27	0.19	0.23	0.08	0.06
Hard GW (pH: 8.1)	0.15	0.49	0.10	0.09	0.23
pH 10.0*	0.01	0.02	0.04	0.04	0.02

*: pH of DDW was adjusted by high purity HCl or NaOH.

Table 5.20: Total zinc mass (mg) leached from tires after 28 days

Leaching Solutions	Tire Chips				
	Crumb	1"×1"	2"×2"	4"×2"	6"×2"
Rainwater (pH: 3.0)	79.43	2.46	2.50	2.13	2.66
pH 4.0*	72.97	1.07	1.15	0.97	1.35
Soft GW (pH: 6.3)	50.74	0.52	0.33	1.40	0.51
pH 7.0*	33.79	1.06	0.59	0.66	0.98
Hard GW (pH: 8.1)	14.83	0.20	0.78	0.41	0.41
pH 10.0*	0.31	0.08	0.20	0.16	0.65

*: pH of DDW was adjusted by high purity HCl or NaOH.

Table 5.21: Total aluminum mass (mg) leached from tires after 28 days

Leaching Solutions	Crumb	Tire Chips			
		1"×1"	2"×2"	4"×2"	6"×2"
Rainwater (pH: 3.0)	3.02	0.14	0.26	0.16	0.28
pH 4.0*	0.21	0.37	0.26	0.38	0.25
Soft GW (pH: 6.3)	0.03	0.01	0.01	0.01	0.01
pH 7.0*	0.05	0.01	0.01	0.02	0.02
Hard GW (pH: 8.1)	0.07	0.05	0.06	0.04	0.06
pH 10.0*	0.73	0.31	0.35	0.29	0.24

*: pH of DDW was adjusted by high purity HCl or NaOH.

The highest leaching for all four metals occurred under acidic conditions, except for aluminum leaching was comparable under acidic and basic conditions. For iron and aluminum, minimal leaching was observed under neutral pH conditions, the only exception was the iron leaching from soft groundwater. For zinc and manganese, there was a continuous decrease of leaching with the increasing pH.

Iron and aluminum concentrations measured in leachate solutions were above their solubility limits in DDW. For instance, the iron concentrations by the end of the first week in pH 4.0, 7.0 and 10.0 solutions (for chip size 1"×1") were 19.627, 0.011 and 0.075 mg/L respectively. This indicates chelating between the leaching organics and iron. It appears that chelating of organics was more favorable with iron at acidic conditions because there was a high degree of organic leaching from scrap tires at high pH values, but this did not result in high iron concentrations in the leachates.

Elevated levels of metals at acidic conditions can be an aesthetic issue since they are listed in the USEPA drinking water regulations [EPA, 2009[a]]. It was observed that iron and manganese in these batch experiments exceeded their corresponding MCLs

listed in NSDWR under acidic conditions (pH 4.0 or lower). Zinc exceeded its MCL in samples coming from crumb rubber at pH lower than 7.0. Only for few samples, manganese concentration was above its MCL at neutral pH conditions. On the other hand, aluminum exceeded its MCL for few samples under extreme pHs (under acidic and basic conditions). It should be noted that the comparison with MCLs were made for the results of batch experiments conducted in this study. In practical applications, the exceedences of MCLs will depend on the amount of tire chips placed and the volume of water to be mixed with. These results indicate that iron and then manganese at the two elements important to monitor.

All the elements measured in the leachates can be related to the manufacturing information for tires summarized in the previous chapter. The presence of zinc is related to the rubbery portion of tire, while the presence of iron is mainly related to the wires inside the tires [Cummings, 1998; RMA, 1998]. Leaching of iron from crumb rubbers was significantly lower than leaching from tire chips at all pH conditions. Since metals were removed from the crumb rubbers, the only source of iron is the iron oxide which is added as an additive during the manufacturing process [Cummings, 1998]. There is also a possibility of some residual irons from the wires in the crumb rubber. Besides iron and zinc, the presence of manganese and aluminum was attributed to the wires in tires.

Calcium, Magnesium, Potassium and Sulfur:

The cumulative masses for calcium, magnesium, potassium and sulfur leached from tires are given in Tables 5.22 to 5.25.

Table 5.22: Total calcium mass (mg) leached from tires after 28 days

Leaching Solutions	Tire Chips				
	Crumb	1"×1"	2"×2"	4"×2"	6"×2"
pH 4.0*	82.19	2.33	5.42	6.64	4.21
pH 7.0*	41.53	4.98	6.93	10.03	2.75
pH 10.0*	13.46	1.88	5.54	4.34	1.42

*: pH of DDW was adjusted by high purity HCl or NaOH.

Table 5.23: Total magnesium mass (mg) leached from tires after 28 days

Leaching Solutions	Tire Chips				
	Crumb	1"×1"	2"×2"	4"×2"	6"×2"
pH 4.0*	9.91	0.17	0.13	0.13	0.11
pH 7.0*	2.05	0.14	0.14	0.21	0.07
pH 10.0*	0.82	0.10	0.19	0.14	0.08

*: pH of DDW was adjusted by high purity HCl or NaOH.

Table 5.24: Total potassium mass (mg) leached from tires after 28 days

Leaching Solutions	Tire Chips				
	Crumb	1"×1"	2"×2"	4"×2"	6"×2"
pH 4.0*	1.96	1.75	0.76	1.01	0.48
pH 7.0*	1.53	0.87	0.64	0.80	0.23
pH 10.0*	1.48	1.16	0.44	1.13	0.24

*: pH of DDW was adjusted by high purity HCl or NaOH.

Table 5.25: Total sulfur mass (mg) leached from tires after 28 days

Leaching Solutions	Tire Chips				
	Crumb	1"×1"	2"×2"	4"×2"	6"×2"
pH 4.0*	5.16	1.24	0.89	1.00	0.96
pH 7.0*	4.61	1.52	1.13	1.09	0.98
pH 10.0*	4.96	1.78	1.32	1.60	1.10

*: pH of DDW was adjusted by high purity HCl or NaOH.

Highest leaching for calcium and magnesium occurred under acidic conditions from crumb rubber, there was no clear pH effect for the tire chips. Potassium and sulfur leaching stayed constant over the pH range for both crumb rubber and tire chips. For most of the cases, the amounts of leaching were in the order of calcium>>magnesium-sulfur>potassium (the order of magnesium and sulfur changes depending on) for crumb tires, and calcium>sulfur≥potassium>magnesium for tire chips.

Leaching Rate of Inorganics:

The cumulative leaching rate of four metals at acidic conditions is shown in Figure 5.17. A rapid initial leaching rate was observed for zinc, followed by a slower but constant rate, while there was a constant rate of leaching for iron, manganese and aluminum from the beginning of the experiments without showing any sign of slowing down. This observation was attributed to the release of the zinc from the rubbery portion of the tires due to the relatively similar leaching patterns observed for dissolved organics and zinc (Figures 5.15 and 5.17). On the other hand, iron, aluminum and manganese are probably coming from the wires in the tire chips showing a continuous and a constant rate of dissolution.

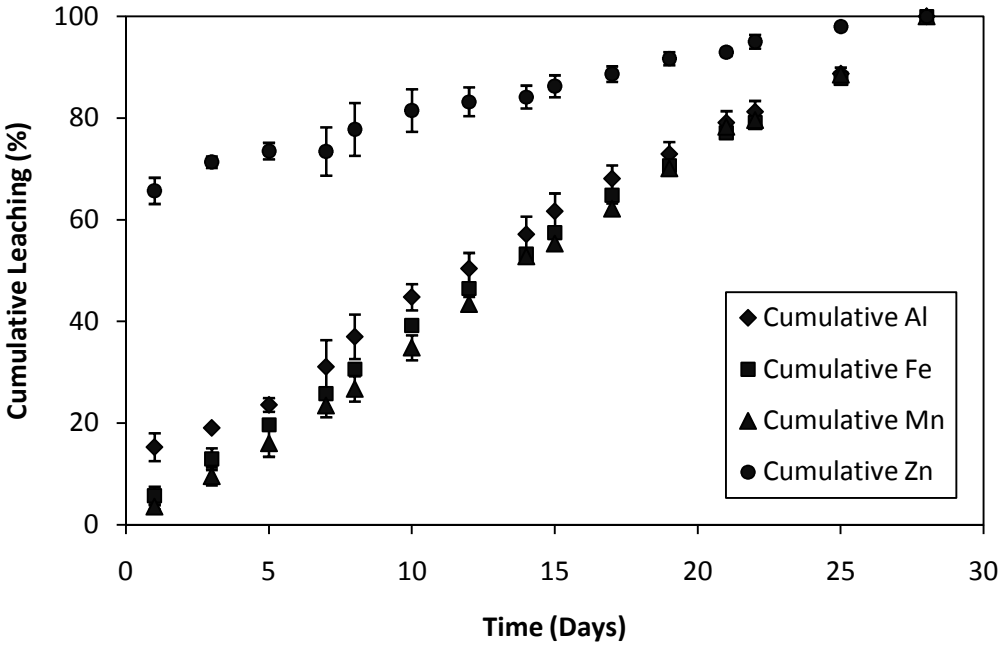


Figure 5.15: An example cumulative plot of metals leaching trend (e.g., chip size 1"×1" in pH 4.0 solution) (E.2)

Overall Evaluation:

These results showed that as for organics, using tire chips at neutral pH conditions will minimize leaching of inorganic constituents from tires. While leaching of detected eight elements from scrap tires is relatively low at basic conditions, their concentrations significantly increases at acidic conditions, especially for iron, zinc and calcium. Among the analyzed other elements, As, Cd, Cr, Cu, Mo, Se, Ni and Pb were below the detection limits. Thus, scrap tires are not likely to affect water quality for the compounds that are listed in NPDWR. Iron, manganese and zinc were observed at concentration exceeding their corresponding MCLs depending on the tire type/size and pH of the water (especially acidic conditions). There was also no clear impact of particle size on the leaching of

metals from tires. Therefore, in the field applications, the priority should be given to monitor these metals (iron, manganese and zinc) to assess their impacts on the water quality in the water sources.

TCLP Tests

In this study, a set of TCLP tests was also conducted for the tire samples. During these tests, only a group of selected inorganic parameters in the TCLP list was monitored. The average concentrations of the TCLP parameters and their regulatory limit are shown in Table 5.26.

Table 5.26: Average concentrations in the extract (mg/l)

TCLP Parameter	Regulatory Limit (mg/l)	Tire Chips				
		Crumb	1"×1"	2"×2"	4"×2"	6"×2"
Arsenic	5.0	0.007	0.003	0.003	0.003	0.006
Barium	100.0	NA	NA	NA	NA	NA
Cadmium	1.0	0.003	0.002	0.002	0.002	0.001
Chromium	5.0	0.002	0.019	0.003	0.007	0.008
Lead	5.0	0.056	0.007	0.034	0.018	0.021
Mercury	0.2	NA	NA	NA	NA	NA
Selenium	1.0	ND	ND	ND	ND	ND
Silver	5.0	NA	NA	NA	NA	NA

ND: Not Detected.
NA: Not Available.

Based on the data presented in Table 5.27 the leachates from the tires contain 100 to 1000 times lower concentration than the regulatory limits. This is consistent with the previous studies [Downs et al., 1996; Zelibor, 1991; Ealding, 1992; Al-Tabbaa and Aravithan, 1998]. Thus, it can be concluded that based the current regulations tires can be

considered as a non-hazardous waste. Since, current ICP analysis method measures a range of elements, data for these compounds are also given on the following page (Table 5.27). Among all the elements only Na is not presented since TCLP extract contains a significant amount of sodium in the background

.

Table 5.27: Analysis of TCLP extract (mg/L)

Element	Crumb	1"×1"	2"×2"	4"×2"	6"×2"
Al	0.155 ± 0.004	NA	0.037 ± 0.002	0.039 ± 0.003	0.022 ± 0.005
As	ND	ND	ND	ND	ND
Ca	38.321 ± 9.425	0.733 ± 0.014	2.286 ± 0.277	4.549 ± 1.506	1.559 ± 0.750
Cd	0.003 ± 0.000	0.002 ± 0.001	0.002 ± 0.001	0.002 ± 0.001	0.001 ± 0.000
Cr	0.002 ± 0.000	0.019 ± 0.001	0.003 ± 0.001	0.007 ± 0.005	0.008 ± 0.003
Cu	0.047 ± 0.001	0.215 ± 0.040	0.032 ± 0.011	0.017 ± 0.009	0.072 ± 0.007
Fe	1.221 ± 0.029	151.704 ± 3.816	13.404 ± 4.493	21.427 ± 10.212	44.977 ± 10.360
K	1.628 ± 0.032	0.940 ± 0.008	0.892 ± 0.005	0.920 ± 0.035	0.975 ± 0.074
Mg	1.944 ± 0.237	0.042 ± 0.004	0.051 ± 0.003	0.113 ± 0.050	0.051 ± 0.016
Mn	0.226 ± 0.037	0.823 ± 0.038	0.093 ± 0.023	0.152 ± 0.038	0.249 ± 0.047
Mo	ND	ND	ND	ND	ND
Ni	0.005 ± 0.000	0.013 ± 0.003	0.003 ± 0.001	0.008 ± 0.004	0.004 ± 0.001
P	0.056 ± 0.001	0.016 ± 0.001	0.017 ± 0.001	0.021 ± 0.008	0.012 ± 0.001
Pb	0.056 ± 0.007	0.007 ± 0.002	0.034 ± 0.003	0.018 ± 0.012	0.021 ± 0.004
S	1.774 ± 0.059	0.485 ± 0.075	0.309 ± 0.001	0.362 ± 0.009	0.306 ± 0.000
Se	ND	ND	ND	ND	ND
Zn	25.780 ± 0.117	1.638 ± 0.293	0.589 ± 0.042	0.814 ± 0.306	0.800 ± 0.009

NA: Not Applicable.
ND: Not Detected.

CHAPTER SIX

CONCLUSIONS AND RECOMMENDATIONS

The following are the major conclusions for each objective of this study:

Objective 1: Investigate the effect of aqueous chemistry on the leaching of organic and inorganic constituents from tires

The best condition for using scrap tire chips in environmental reuse applications was found to be around the neutral pH conditions. Leaching of dissolved organic carbon and selected elements was minimal around the neutral pH values. pH was a more important parameter than conductivity of the solution in controlling the leaching of DOC and selected elements from scrap tires. The changes in conductivity did not have a significant impact on the leaching of organics or inorganics. When tire chips were exposed to acidic conditions, iron by far was the most significant metal leaching from tires at very large quantities (up to ~800 mg/ 100 g tire). The presence of organics significantly increased the iron concentrations in water (e.g., ~ 20 mg/L at pH 4.0) above its solubility (i.e., ~0.03 mg/L at pH 4.0) in DDW. Manganese was the second metal observed leaching at acidic conditions; however at amounts (2-5 mg/ 100 g tire) significantly lower than iron. When the tire chips were exposed to basic conditions, the leaching of DOC significantly increased, reaching (27 mg/ 100 g tire). For crumb rubber, leaching of DOC reached up to ~120 mg/ 100 g tire, indicating that organic components in tires are more prone to leaching under basic conditions. Under the basic conditions, the

leaching of each monitored element, including iron (<1 mg/ 200 g tire), were significantly lower. The results also showed that As, Cd, Cr, Cu, Mo, Se, Ni and Pb were always below the detection limits for all conditions tested during one month of leaching experiments.

Objective 2: Examine the leaching of total dissolved organic carbon and dissolved nitrogen from tires

As mentioned before, the leaching of DOC from tires were highest at the basic conditions. Only at the most acidic condition tested in this study (pH 3.0), the leaching of DOC from tire chips approached to the amount leached at basic conditions (24.5 mg DOC /100 g tire at pH 3.0 vs. 27 mg DOC/ 100 g tire at pH 10). It was visually observed during the filtration of the samples, there was an increasing amount of black residues on the membrane filter with decreasing pH, especially at pH 3.0. This indicates that lowering pH to very low values increasingly deteriorates the physical structure of tires. Therefore, it is possible that more severe leaching of DOC may occur from tires if exposed at very acidic conditions.

The $SUVA_{254}$ values of the leaching solutions remained in the range of 1.5 to 3.0 L/mg-m during the experiments. A gradual increase in the $SUVA_{254}$ values after the first week was observed, indicating an increase in the fraction of aromatic carbons leaching from the tires over time. This increase was no more than one unit, except rainwater samples. This trend suggested that some non-aromatic (e.g., aliphatic) compounds were dissolved quickly at the beginning of the leaching experiments, which was followed by dissolution of more aromatic components with time. During the most acidic leaching

experiments (pH 3.0), the initial $SUVA_{254}$ values were recorded at 5.0 and increased up to 12.0 L/mg-m with time. This was attributed to the rapid deterioration of the integrity of tires under very acidic conditions, as discussed above. The presence of some aromatic compounds in the leachate solution was determined with GC/MS/MS scans. Some of these compounds (e.g., aniline, benzothiazole, benzothiazolone) have been also reported in previous studies. Consistent with DOC data, a larger group of compounds was detected at pH 10.0 than other pH conditions.

Leaching of DN (1-3 mg/ 100 g tire) from tires was significantly lower as compared to DOC and remained in dependent of pH.

Objective 3: To quantify the leaching of organics and inorganic constituents from scrap tires as a function of time during one month period

The overall amounts of organic and inorganic constituent leaching from scrap tires were summarized in the conclusions listed for the first two objectives above.

Analysis of DOC leaching data also showed that the mass of DOC leached during the first 12 hr consisted of 40-50% of the leaching during the first week and 20-25% of the leaching during the four weeks of experiments. Although the cumulative DOC mass leached from tires depended on tire size and leaching solution, the leaching rate remained constant regardless of tire type and leaching solution.

Analysis of leaching rate of four metals (Zn, Fe, Al, Mn) at acidic conditions showed a rapid initial leaching rate was observed for zinc, followed by a slower but constant rate, while there was a constant rate of leaching for iron, manganese and aluminum from the beginning of the experiments without showing any sign of slowing

down. This observation was attributed to the release of the zinc from the rubbery portion of the tires due to the relatively similar leaching patterns observed for DOC and zinc. On the other hand, iron, aluminum and manganese are probably coming from the wires in the tire chips showing a continuous and a constant rate of dissolution.

Objective 4: To examine the effect of particle size on leaching

Crumb rubber showed significantly higher degree of leaching for all detected constituents except iron, since the main source of the iron in tire chip was the wires that were removed prior to preparing the crumb rubber. Among the tire chips that are within the particle size range of practical applications, leaching from 1"×1", tire chips, in general, was higher than the other particle sizes. The difference of leaching from tire chips of 2"×2", 4"×2" and 6"×2" was relatively small or negligible.

- ***Other findings***

The average BET surface area and total pore volume of triplicate tire samples were 0.9596 ± 0.0573 m^2/g and 0.000733 ± 0.000055 cm^3/g, respectively. The results indicated that that the tires are non-porous materials, and leaching from tires occurred primarily from their external surfaces. The ash content of the tire chips and crumb tires were 20.94 and 6.64 %, respectively. Elemental analysis showed that 80% of tire composition is carbon, followed by 7% hydrogen, 2.5% oxygen, and 1 % sulfur.

Recommendations for Practical Applications

Based on the results obtained in this study, the following recommendations are provided for practical applications.

- Neutral pH conditions should be preferred for reuse applications. Permanent acidic and basic conditions should be avoided as much as possible.
- Using larger size tire chips (2"×2" or larger) for a constant mass of tire chip will decrease the leaching from tires.
- Pre-washing of tires (e.g. for a duration of 12 hr) prior to reuse applications can significantly reduce the leaching of dissolving organic and inorganic constituents into water sources.
- Removal of metals from the tires wires can significantly reduce the release of iron and some other constituents from tires.

Recommendations for Future Research

Some recommendations for future research are also provided.

- Considering the visible deterioration of tires observed especially at acidic conditions, it will be important to characterize the physical integrity (e.g., tensile strength, elastic modulus) of tire chips to assess their long term use in practical applications.
- There are several organic contaminants identified which are harmful, toxic or carcinogenic in the leachates at basic conditions. As the results of this research indicated, there is a high amount of unidentified organics leaching from tires.

Identification and quantification of specific organic components in the leachates will be important to assess their environmental impact.

- Although laboratory batch experiments, as conducted in this study, provide useful information, column experiments and pilot field studies are necessary to further examine the behavior of tire chips, where a number of complex factors (biological, chemical and physical) affect their behaviors in the environment.

APPENDICES

Appendix A

A.1: News from “USA TODAY”

USA TODAY

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Artificial turf: Health hazard?

By Michael McCarthy and Steve Berkowitz, USA TODAY

Since the 1960s, artificial turf has been installed on sports fields across the nation, touted as a more durable and cost-effective alternative to grass. Early synthetic surfaces — such as the short-bladed AstroTurf — have given way in recent years to longer-bladed versions designed to be softer and help prevent injuries.

But there are increasing concerns that some synthetic fields — particularly fraying AstroTurf surfaces that have been in place for years — are contaminated with lead and could pose a health hazard to children, athletes and others who use them.

A half-dozen artificial fields in New York and New Jersey as much as a decade old or more have been closed because of concern about high levels of lead in the turf fibers.

The threat of lead contamination in old turf has given a fresh platform to those raising red flags about newer types of artificial turf. These surfaces often include bits of recycled tires — known as "crumb rubber" — among the turf blades to provide a cushioned surface. They have been installed at thousands of schools, public parks and indoor sports facilities across the country, and more are scheduled.

The questions about both types of artificial turf have created ripples nationwide, prompting a federal investigation of artificial surfaces and raising anxiety among health and elected officials, some of whom want to ban new installations until government agencies study the potential health risks and environmental hazards.

"They're in high schools, university stadiums, public parks. So it's a public health issue," says Rep. Rosa DeLauro, D-Conn., who helped prompt the U.S. Environmental Protection Agency to get involved. "It is more than the lead issue. It's the crumb rubber" in the new types of turf.

Says New Jersey Assemblyman John Rooney: "A little foresight is worth a hell of a lot of regret down the road."

The artificial turf industry has been trying to reassure current and prospective customers its products are safe while pointing out the newer generation of turf helps find a use for millions of used tires.

So far, the concern about lead is focused mostly on older, nylon fields built by AstroTurf's former U.S. owner, Southwest Recreational Industries, which went out of business in 2004. During a news conference Monday in New York, the current marketers of AstroTurf said their products and those marketed by Southwest Recreational Industries are safe.

"In the last couple of weeks, the science (showing turf is safe) is being trumped by the perception, the fears, the uncertainty and doubts," said Jon Pritchett, chief executive officer of GeneralSports Venue (GSV), the exclusive licensee for AstroTurf in the USA.

The closed fields include four New Jersey surfaces — in Jersey City, Newark, Hoboken and at the College of New Jersey in Ewing — as well as a high school field in Cicero, N.Y., that were found to contain high levels of lead. Another closed high school field in Liverpool, N.Y., is being tested.

New Jersey health officials discovered the lead, used in pigment to color some fields, in the turf fibers. Kids and athletes could be exposed by inhaling or swallowing lead-laced turf fibers or "dust" kicked up by those playing on the fields, state epidemiologist Eddy Bresnitz says.

There have been no known cases of illness attributed to the fields, but at least four of the closed fields will be torn up and replaced with new artificial surfaces.

Elsewhere, towns have begun limiting access to artificial turf fields by young children, who are most at risk from exposure to lead, which can cause brain damage and even death.

In Montville. N J . for example. kids under 7 will not be permitted to play on two artificial turf fields that registered unsafe lead levels. pending further testing township administrator Frank Bastone says

Children under 6 are "most at risk from exposure to lead." says Dale Kemery of the EPA. which along with the U S Consumer Product Safety Commission (CPSC) has launched an investigation of artificial turf fields

Old turf triggers questions

The original AstroTurf installed at the Astrodome in Houston in 1966 was a hard. carpet-like surface It quickly spread throughout the NFL and Major League Baseball because it gave multi-use stadiums a consistent playing surface and was easier and cheaper to maintain than grass

Today. those old rugs have largely fallen by the wayside in stadiums used by professional and college teams The carpets have been replaced in such arenas by natural grass and newer. more sophisticated types of artificial turf

However. at some smaller stadiums used by high schools. on playgrounds and other places. old AstroTurf remains

The newer fields usually are made from polyethylene and polypropylene. plastics commonly used to make everything from grocery bags to food containers. as well as nylon or a mix of materials The fields mimic the look. feel and footing of natural turf. and they often feature longer strands of plastic "grass" and crumb rubber from recycled car and truck tires These tiny bits of infill provide a springy cushion for kids and weekend warriors and can be kicked up just like dirt on a natural grass field

The national investigation by the CPSC and the EPA will focus on all kinds of turf. not just nylon. CPSC spokeswoman Julie Vallese says The agency already is collecting turf samples and expects to issue a report by early summer "Our focus is on the risk to exposure from lead." Vallese says

Meanwhile. the concern over fake turf has triggered efforts by legislators in five states to get studies of potential health and environmental hazards done Several schools and municipalities nationwide also are testing their fields

There are 3.500 full-size. artificial fields in the USA. estimates Rick Doyle. president of the Synthetic Turf Council. a trade group Such turf accounts for 900 to 1.000 installations a year but does not include smaller surfaces such as practice fields and playgrounds

DeLauro and other officials worry about kids and athletes inhaling or swallowing the small rubber pellets Environmentalists also have cited the pellets as a concern. questioning whether compounds from recycled tire rubber can run off the turf and pollute rivers. lakes, streams and groundwater

Some colleges. including Ohio State and Western Carolina. are having their synthetic fields tested

Separate bills in the New York. New Jersey and California legislatures would ban the installation of new fields until the completion of comprehensive health and environmental studies

Connecticut Senate Minority Leader John McKinney said Wednesday that he is working with the commissioners of the state's departments of public health and environmental protection to find a way to use existing funds for a study In New York City. Public Advocate Betsy Gotbaum has called for an "immediate moratorium" on turf installations until the city completes a study on their "adverse" health effects

Responding to a request from California State Sen Abel Maldonado. Attorney General Jerry Brown's office says it will study whether signs should be posted near synthetic fields warning that users could be exposed to toxic chemicals The California Integrated Waste Management Board has told Maldonado it plans to evaluate whether crumb rubber fields release dangerous chemicals — or cause abrasions and bacterial infections more serious than those occurring on a natural surface A bill by Minnesota State Rep Phyllis Kahn also calls for a health study on the impacts of crumb rubber use

Risks overblown, industry says

The artificial turf industry says the controversy is based mostly on scientifically flawed attacks and sensationalized claims of the risks associated with turf At least one coach agrees that the issue has been blown out of proportion

"Nobody talks about all the radon in the soil. and there are kids playing on that every day. breathing it in." says Mark Zimmerman. an assistant football coach at McQueen High School in Reno

One artificial turf maker is changing its manufacturing process to remove potential toxins

Stephen P Noe. president and CEO of Sportexe Construction Services. which has installed more than 200 full-size fields in the last three years. recently posted a note on the company's website saying "a few colors" of its products "were produced using low levels of lead chromate-based pigments Going forward Sportexe will not be offering these heavy metal based color choices We intend to substitute alternative colors based on non-heavy metal based pigments Although we do not see a health risk in the current products. we believe that this is the best decision for all of our constituents "

GeneralSports Venue owner Michael Dennis says he has a contract to rip up the closed field in Newark and replace it with a new "PureGrass" system with lead-free nylon fibers The

company also will install a lead-free artificial baseball field in the city

Shira Miller, a spokeswoman for the Synthetic Turf Council, said via e-mail Wednesday that manufacturers have been coming together to share information about standards and. "The STC welcomes the involvement of the Consumer Product Safety Commission, the EPA and other groups since we are confident their scrutiny will answer the question of safety issues once and for all."

FieldTurf Tarkett dominates the artificial turf industry with 1,900 U.S. fields. Ten NFL teams play their home games on the company's products. The Montreal-based company has won the contract to replace the closed field at Hoboken's Frank Sinatra Park. The polyethylene FieldTurf surfaces checked by New Jersey health officials contained trace amounts of lead and were deemed not harmful

FieldTurf executives are frustrated that their polyethylene products keep getting lumped in with nylon fields built by a company that's no longer in business

"Our fields were tested and found to be about 50 times below what the U.S. Consumer Product Safety Commission allows in Mr. Potato Head or in Lego," CEO Joe Fields said in a statement

That's good news. New York state Sen. Jim Alesi says. But he wants more proof before accepting the opinion of manufacturers or industry-paid scientists. "We need to have someone that's not *selling* us the product tell us that it's safe," he says. "If what they're saying is believable, then there's nothing wrong with the old Ronald Reagan approach: trust but verify."

The New York Department of Environmental Conservation has launched a study to "assess the potential environmental impact from crumb rubber as an infill material," spokeswoman Lori O'Connell says

The upfront costs to install a synthetic field run from $400,000 to several million dollars. But the fields can last 10 years or more and withstand the kind of non-stop pounding that would turn a natural grass field into dirt

The operator of at least one of the fields closed recently says he has "no choice" but to replace it with another synthetic surface. Densely populated urban areas have to use artificial fields, says Bob Hurley, director of parks and recreation for Jersey City, which has shut down its 11-year-old AstroTurf field in Cochrane Stadium at Caven Point after finding lead during testing

The fake grass allows local teams to "play twice as many" football, baseball and soccer games, says Hurley, a well-known high school boys basketball coach at St. Anthony. "If it rains, half an hour later everything has soaked through and we're able to play."

Jeff Tittel, director of the Sierra Club of New Jersey, says public officials and educators should be in the business of protecting children, he says, not squeezing in as many games as possible

Says New York City's Gotbaum: "If there's no potential long-term or short-term effects that aren't too serious, we'll be the first to get out there and say, 'Hey, it's OK. Everybody get out and play.' I'll be the first person to do that. But I'm not there yet."

Contributing: Tom Ankner, Tehani Schneider and Abbott Koloff of the (Morristown, N.J.) Daily Record; Chris Joyner of The (Jackson, Miss.) Clarion-Ledger; Matthew Daneman of the Rochester (N.Y.) Democrat and Chronicle; Jordan Schrader of the Asheville (N.C.) Citizen-Times; Jeff Martin of the (Sioux Falls, S.D.) Argus Leader; Jeff Delong of the Reno Gazette-Journal

A.2: News from “FOX RENO”

foxreno.com

EPA Reconsiders Use Of Shredded Tires On Playground Surfaces

Posted: 9:19 am PDT June 4, 2009Updated: 12:05 pm PDT June 4, 2009

SAN FRANCISCO -- For years, the Environmental Protection Agency has endorsed the recycling of ground-up tires to cushion the surfaces of children's playgrounds and sports fields -- the same material used for the Obama family's new White House playground.

Now, the agency is having second thoughts.

EPA scientists are worried that they don't have enough information about potential health risks from chemicals in the rubber material, which is popular because it decreases playground injuries and is low maintenance and weatherproof.

The concerns are disclosed in internal agency documents about a study the EPA is conducting of air and surface samples at four fields and playgrounds that use recycled tires. The study was prompted by other research suggesting potential hazards from repeated exposure to bits of shredded tire that can contain carcinogens and other chemicals, according to the documents.

The EPA scientists cited gaps in scientific evidence, despite other reviews showing little or no health concern. They urged their superiors to conduct a broad health study to inform parents on kids' safety.

Results from the agency's limited study, which began last year, are expected within weeks.

"From everything I've been able to see, I'm not sure there's an imminent hazard but it's something we're investigating," said Michael Firestone, EPA's head of children's health protection. "It's critical to take a look at all the data together."

The government has not decided if broader testing is necessary.

Communities from New Jersey to Oregon have raised concerns about children touching, swallowing or inhaling lead, metals and chemicals like benzene, zinc and breathable particles from synthetic fields and play yards.

Last week, New York state officials said they found no significant health or environmental concerns in a study of leaching and breathable air above sports fields with so-called tire crumb -- tiny rubber infill pellets that help anchor the synthetic grass blades. Other local studies have reached similar conclusions, examining artificial grass or tire crumb. Several have recommended more research.

"If they really find it's something toxic, I would be concerned," said Alejandro Arroyo, a teacher watching his high school students from June Jordan School for Equity play soccer at San Francisco's Crocker Amazon Park. The scent of tire rubber wafted over the busy, five-field complex as a dozen third-graders flopped onto artificial turf infused with gravel-sized, black rubber.

"We practice here, we eat lunch here," Arroyo said. "Everybody does that. It's a family park."

Scrap tire mulch cushions the ground under the play set that President Barack Obama's daughters use at the White House. It was recommended by the National Recreation and Park Association, which relies on

the industry's safety assurances and recommendations by the Consumer Product Safety Commission for cushioning the impact of falls, said Richard Dolesh, public policy officer for the park association.

But New York City officials say their new sports fields will no longer use tire crumbs. Connecticut asked the EPA to study the matter shortly after EPA's Denver regional office recommended the same.

The EPA memo was sent to Washington from the Denver office in January 2008, saying that until more was known, the EPA should take a neutral stance instead of sanctioning recycled tires for play areas. The documents, obtained under the Freedom of Information Act, were provided to The Associated Press by the Public Employees for Environmental Responsibility, an advocacy group that objects to the EPA's endorsement of using recycled tires without a broad scientific risk evaluation.

"It appears that there are valid reasons to take a broader perspective of all potential risks associated with crumb rubber" through a full-blown health study, said the memo from Assistant Regional Administrator Stephen Tuber.

Withdrawing the EPA's endorsement would be premature, said EPA spokesman Dale Kemery.

"Nobody has the evidence at this point" to scientifically justify pulling back, he said.

Along with its own research, the agency will consider studies in New Jersey, California, Connecticut and New York to determine whether more testing is needed. A shortcoming of EPA's study is the small number of locations examined, according to the documents.

The Synthetic Turf Council, an advocacy trade group, says laboratory-based claims of toxicity don't reflect actual conditions.

"The science is clear that synthetic turf crumb rubber infill fields do not present a human health or environmental risk," said Rick Doyle, president of the group.

The CPSC concluded last summer that synthetic fields pose no lead hazard for kids. It tested turf fibers for lead at a few fields. It did not examine chemicals in tire crumbs interspersed with the turf, or playgrounds where children handle mulch made from shredded tires.

A health advisory from the federal Centers for Disease Control and Prevention said older fields may be riskier for lead as wear kicks up turf dust. Not all turf fibers contain lead. The CDC urges eliminating all nonessential uses of lead, which can cause neurological damage in children.

Chemicals in recycled tires could vary by location because tire manufacturers differ, EPA scientists said.

Rep. Rosa DeLauro, D-Conn., who had criticized the CPSC's effort and pressed the EPA for a comprehensive investigation, welcomed the environmental agency's role.

"This is not about creating panic among parents or calling for the closure of fields made from synthetic turf," she said in an e-mail. But people "need accurate answers about the safety and health effects of these fields to make the best possible decisions about where children and others are playing."

A.3: News from “Red Green and Blue”

Red Green ... Blue

Red, Green, and Blue

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White House Playground Covered With Harmful Mulch, Says Environmental Group

Written by Amanda Peterka
Published on April 7th, 2009 in Leader, Natural Resources, U.S

4 Comments

The Obamas may have planted a fresh and healthy garden on the White House lawn, but their playground for the kids is anything but healthy, according to an environmental-health group.

Environment and Human Health contends that the used-tire mulch covering the playground causes skin and eye irritation and destroys mucus membranes, reports the Seattle Times. The group cites a review done by Sinai Hospital in New York in March that reported that playgrounds made from used tired tend to get very hot and can cause kids to get skin infections and inhale toxins and carcinogens.

A spokesperson for Michelle Obama, however, said they just followed recommendations from the National Recreation and Park Association, which in turn followed those from the International Play Equipment Manufacturer's Association, which listened to the Rubber Manufacturer's Association. The president of the latter "pointed to a series of studies in the U.S. and in Europe — which has reused scrap tires for much longer than the United States has — that show tires are safe," according to the Los Angeles Times.

When I tried to do a simple Google search on used-tired mulch, I got conflicting results. The first site told me that it is "The Perfect Rubber Mulch for Playgrounds, Landscapes, and Equestrian." The second site says it's "deadly." The rest of the results continue in much the same pattern. It's either the miracle or murderous mulch, and not much in between.

>>See also: *7 Ways to Kick Back at the White House*

Should the Obamas be trusting something as seemingly contradictory as this for their young children? Cities have been using this mulch in parks for more than a decade now. Chicago carted in 30 tons of rubber mulch in the fall of 1995 to decorate its natural areas. The reasons for using the mulch are that it is heavier than wood chips, so it's less likely to blow away, and it is, of course, made from recycled tires.

Unless children are rolling around in the stuff every day (then again, they might be), I don't see much wrong with them merely running on the ground. The Obamas seem to agree.

Photo Credit: The White House playground, Rubber Mulch at Flickr under a Creative Commons License

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Tags: carcinogens, irritants, Obama, playground, rubber mulch, used-tire mulch

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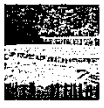

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4 Comments

1 1

Julie Cole said on April 9th, 2009 at 11:24 pm

Perfect Rubber Mulch Replies To The Rubber Mulch Safety Issue

We found your article particularly interesting since we are the company that sells the "Perfect Rubber Mulch" that you mention in your article. Rubber mulch has been heavily scrutinized with stringent private and government testing and has proven to be a safe, 100% recycled alternative to bark mulches that decompose over time and compact. Please see the studies outlined below on rubber mulch safety and its toxicity. We hope the studies done by Mayo Clinic and Consumer Product Safety Council will lend some credibility to dispel the unsubstantiated, invalidated by any studies, nonsense out there about rubber mulch.

We too have run across the few "internet experts" taking shots at the safe use of rubber mulch and are well aware that they are making blanket false statements with no test results to prove anything they say on rubber mulch and how harmful it may be. It is slanderous and will be addressed through the proper channels, not on their personal YouTube sites and other fly by night internet quacks that spew their reckless slander. If left up to the thinking of these so called "internet experts" every bit of land butting up to any highway or byway in the USA would be an EPA nightmare from the tires losing tread daily, year after year. People need to research and use common sense in their search for the "Perfect Rubber Mulch" for their playgrounds. The data and research outlined below is a good start. Read for yourself these studies before believing and printing articles that bring into question the safety of rubber mulch. We sell millions of pounds of safety rubber mulch to schools, daycares and yes, even the US government for training pits for hand- to- hand combat. Rubber mulch is being mandated in many areas as the SAFEST alternative under play equipment for our children. Rubber mulch may not be for everyone as it is expensive compared to bark mulches, but not because of safety issues. Obviously the Obama's have done their homework and found rubber mulch a perfect rubber mulch to create a safe play environment for their children at their new home in the White House as have thousands of schools, daycares and homeowners.
Below are the FACTS that can be substantiated about rubber mulch.
Thank you for the opportunity to respond to your article.

Julie Cole-Owner
PRM Enterprises LLC
Perfect Rubber Mulch

This article is a excerpt from the "Handbook for Public Playground Safety", Pub. No. 325
U.S. Consumer Product Safety Commission, Washington, DC 20207
Another source for information is the Consumer Product Safety Commission at this link:
http://www.cpsc.gov/cpscpub/pubs/327.html

Toxicity

Rubber mulch is considered non-toxic. MSDS Sheets for key components available upon request. Based on Toxicity Characteristic Leaching Procedure (TCLP) conducted on scrap tire chips (method 1311 of USEPA), the following trace metal elements were determined to be significantly lower than regulatory threshold limits: Arsenic (As), Cadmium (Cd), Chromium (Cr), Lead (Lb), Selenium (Sc), and Silver (Ag). Source: Criteria of Selecting Toxicity Characteristic Leaching Procedure (TCLP) and Synthetic Precipitation Leaching Procedure (SPLP) Tests to Characterize Special Wastes. Dr. Chih-Shin Shieh, Florida Institute of Technology, June 30, 2001. Oral ingestion is deemed to be low in overall hazard because ingestion of tire crumb on the ground is not likely, and the gastrointestinal tract is unlikely to be efficient in extracting toxic chemicals from tire crumb. Tire crumb does not contain chemicals with high vapor pressures; thus, exposure via inhalation is deemed inconsequential and the resulting hazard negligible. Dermal exposure is deemed to be unlikely and therefore to present low overall hazard. A carrier solvent more efficient than water would be needed to extract toxic chemicals from tire crumb in quantity, and a suitable non-polar vehicle would be required to penetrate protective skin layers for significant absorption. This was deemed implausible in a playground situation. Cancer hazard as measured by relevant in vitro predictive assays, was deemed negative. Ingestion of small amounts of tire crumb by small children will not result in an unacceptable hazard of contracting cancer. Source: Toxicological Evaluation for the Hazard Assessment of Tire Crumb for Use in Public Playgrounds. Journal of the Air & Waste Management Association. 2003 In 1994 the Maryland Environmental Services (MES) sent 3/4 inch pieces of tire chips to a testing laboratory to be tested with hydrochloric acid (stomach acid). "Visual examination of insoluble residue appeared to indicate only fibrous reinforcing strands were dissolved by the hydrochloric acid. The tire rubber did not appear to be affected in any way; i.e. chalking, cracking, spauling, fracturing, etc." (PSI report No. 466-40013-001). Therefore, if a piece of rubber is swallowed, it should not cause any acute or chronic problems. Short-term issues, such as an upset stomach will be a function of the amount of rubber swallowed. As to the fate of the rubber chips swallowed, they are eventually evacuated from the body, just like any other non-digestible material. Source: RubberManufacturers Association
http://www.rma.org/scrap_tires/scrap_tire_markets/playgrounduse.cfm

D. Leaching:A number of studies have been done to determine the potential for leaching from recycled scrap tires and recycled tire products. Increased levels of zinc and iron were found in soil tilled with raw crumb rubber particles (1/4" and less) when tested annually for 4 years. The amounts detected were below levels of concern and posed no hazards to water quality. Additionally no toxicity to turf grass was observed in these studies. Source: Top Dressing with Crumb Rubber on Athletic Fields. Dr. J.N. Rogers, III and J.T. Vanini. Department of Crop and Soil Sciences, Michigan State University. 1994 Zinc that had leached from scrap tires was determined not to pose any potential harm to the environment. Source: Identification of Tire Leachate Toxicants and A Risk Assessment of Water Quality Effects Using Tire Reefs in Canals. Bulletin of Environmental Contamination and Toxicology, 578-581. Environmental Canada. 1994 Some volatile and semi-volatile organic compounds were identified in scrap tire leachates using the TCLP test. Reported levels are far below regulatory limits:

Reported Value ug/L Regulatory Limit ug/L

Carbon disulfide 67 14,400

Methyl ethyl ketone 21 7,200

Toluene 190 14,000

Phenol 46 14,400

Source: A Report on the Use of Shredded Scrap Tires in On-Site Sewage Disposal Systems. Department of Environmental Conservation State of Vermont. Brattleboro, VT. Envirologic Inc. 1990 Chemicals leaching from relative fresh tire crumb may present a moderate toxic threat to aquatic species if the runoff is not diluted However this toxic activity is quickly degraded by natural processes, presumably by conversion of the chemicals responsible to nontoxic products Conditions likely to produce runoff, such as rain and snowmelt, are also likely to dilute the runoff in receiving sewers, bodies of water, and groundwater by considerable volumes Given that undiluted runoff is not likely and that 3 months is an outside estimate of the duration of toxicity, it is doubtful that tire crumb would present a significant risk of contamination in receiving surface waters or groundwater Source: Toxicological Evaluation for the Hazard Assessment of Tire Crumb for Use in Public Playgrounds. Journal of the Air & Waste ManagementAssociation. 2003

2 2

Patricia Taylor said on April 16th, 2009 at 10:03 pm

I would not characterize the doctors, public health professionals and policy experts who compose Environment and Human Health, Inc (EHHI) as "internet experts "

Nancy Alderman, President of EHHI, recently wrote this: "Recycling is good - but there are certain things that should not be recycled We should not recycle asbestos, we should not recycle lead and we should not recycle rubber tires, certainly not where children play "

In addition, Dr Philip Landrigan is eminently well-qualified to comment upon the hazard of products made from recycled rubber tires

Remember that crumb rubber, like chunk rubber and rubber mulch, is made from shredded, ground, or pulverized recycled rubber tires and rubber dust.

Philip J Landrigan, M D , M Sc., the Ethel Wise Professor and Chair of the Department of Community and Preventive Medicine, is a pediatrician, epidemiologist, and internationally recognized leader in public health and preventive medicine He has been a member of the faculty of Mount Sinai School of Medicine since 1985 and Chair of the Department of Community and Preventive Medicine since 1990 Dr Landrigan is also the Director of the Children's Environmental Health Center

Dr Landrigan recently wrote this: "Crumb rubber, a major component of current generation synthetic turf fields, is typically made from ground-up recycled tires containing styrene and 1, 3-butadiene, the major constituents of synthetic rubber Styrene is toxic to the nervous system, and butadiene is a proven human carcinogen "

William Crain is no wingnut Crain is a professor of psychology at The City College of New York. Dr Crain and Dr Jim Zhang, an associate dean and professor of environmental and occupational health at the UMDNJ-School of Public Health, co-authored a recent UMDNJ study that "finds that when children or athletes ingest the tiny rubber granules in synthetic turf, it is likely that a significant portion of the lead in the granules will be absorbed by their bodies' gastric fluids " (See http://www.newswise.com/articles/view/544449/)

From the same article:

"The UMDNJ study included just one 'new generation' artificial fiber While the sample had a relatively low level of lead, the absorption fractions into synthetic gastric and intestinal fluids were still high (34 6 and 54 0 percent, respectively)

William Crain, a co-author on the study and a child psychologist at The City College of New York, said the findings are especially worrisome with respect to young children who might pick up granules and ingest them The granules can also be transported to homes in the shoes of field users, making the granules accessible to young children "Whenever young children are involved, we need to particularly careful, because they are most vulnerable to toxic chemicals," Crain adds

The study also included an analysis of the rubber granules in seven park samples for the presence of polycyclic aromatic hydrocarbons (PAHs) The researchers found that five of the seven samples contained at least two PAHs that exceeded New York State Department of Environmental Conservation safety limits for contaminated soil The PAHs that were found are possible, probable, or known human carcinogens as defined by the International Agency for Research on Cancer The investigators found that the PAHs seemed not to be absorbed into the digestive tract, which should help direct researchers to other potential PAH exposure routes, such as inhalation or skin contact

The investigators also noted high levels of zinc in rubber granules High zinc levels present a special danger to non-human species in the environment " (End of quote)

The other exposure routes, "such as inhalation or skin contact," are routes that would carry PAHs into the lungs and onto the skin of toddlers and children who play on playgrounds and artificial fields every day as part of their regular school day, during recess or gym class, as well as for team sports

Finally, the Attorney General of Connecticut is no extremist Neither is CT Congresswoman Rosa DeLauro In a joint press release from April 28, 2008 DeLauro and Blumenthal called on the Environmental Protection Agency (EPA) to investigate the potential health and environmental impact of synthetic turf fields The EPA agreed to an investigation

The DeLauro/Blumenthal press release states this: "Synthetic turf – commonly used on athletic fields, as well as for children's play areas – can be made of ground, or crumb, rubber from recycled tires The fields are also made of nylon or polyethylene, which is dyed green to create the artificial grass In addition to

health concerns over the use of lead in the dye are the possible effects of carcinogens released into the air from the crumb "

The press release ends with this statement DeLauro and Blumenthal: "The federal government should investigate credible claims about toxic chemicals to confront environmental and public health dangers Schools across the state are replacing grass fields with artificial turf made from recycled ground rubber tires Preliminary tests point to possible troubling health risks, including significant lead levels and carcinogens The federal government needs to tread on this turf — to investigate potential threats including risks of contaminated runoff into rivers and water supplies "

While the industry engages in doubt promotion and character assassination, even as scientists and government officials call for investigation, children are playing on rubber mulch and crumb rubber every day The proof of harm will be borne in their bodies

We need to take better care of ourselves, each other, and especially our children; whose smaller, still developing bodies cannot tolerate contamination without consequence

3 3

Roger Wilson said on June 6th, 2009 at 8:19 am

Ever watched the news and noticed the huge black cloud and the toxic run off from a rubber tire fire After all, tires are made with petroleum These fires are very resistant to the efforts of fire fighters and now that we are talking heat, the temperature from direct sunlight can raise the surface temperature of this product to well over safe levels This can easily cause severe burns to the human anatomy
The expense of this rubber product is over the top and beyond the reach of most homeowners and neighborhoods Compare to wood chips You can get the chips free The tree companies have to pay to landfill their chip waste The tree companies will deliver and place the product at your direction After a few years of outdoor seasoning, you dig it up and spread the composted mulch around your yard and trees or neighborhood to improve the soil quality Give it to others Now, it is time to begin the process once again

Yep, thats it call the tree company for free wood chips GREEN GREEN, GREEN! Now thats really recycling at its very best Lets all do our little bit to help our earth

Your friend

Roger

4 4

JOE LIPTOW said on June 23rd, 2009 at 11:18 am

Aside from the toxicity issues which may or may not be a legitimate health concern regarding recyled tire use in play/sport surfaces, there is also a heat retention and balance issue I recently walked on chunked rubber mulch that was around 4" deep and found it disturbing and harder to balance on Let's not go recycle crazy if the application does not improve or at least equal the current state of the art For me, I can't see to many ways to improve upon steel and wood playgrounds with natural mulch footing Rubber crumbs in artificial sport fields are a different situation Maybe the best use of rubber tire mulch would be for large scale areas requiring weed suppression Does anyone know what the greatest use to date is of recycled tire material?
Joe Liptow - LEED AP

Appendix B

Figure B.1: Crumb rubber

Figure B.2: Tire chips (size 2"×2") before the leaching experiment

Figure B.3: Bottle with tire chips (size 2"×2")and the leaching solution

Figure B.4: Tire chips (Size 2"×2") after the leaching period (leaching solution at pH 4.0)

Appendix C

Table C.1: Surface area and pore volume analysis results

Analysis Number	BET Surface Area (m^2/g)	Pore volume (cm^3/g)
1	1.0169	0.000753
2	0.9285	0.000688
3	0.9335	0.000758
Average Values	0.9596 ± 0.0573	0.000733 ± 0.000055

Table C.2: Elemental analysis results (%)

Analysis Number	Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen	Ash
1	80.71	7.27	0.35	0.94	2.60	8.12
2	76.74	7.15	0.38	1.22	4.11	10.40
3	82.49	7.46	0.49	1.07	2.33	6.16
4	82.11	7.43	0.50	1.01	0.83	8.12
5	80.93	7.21	0.41	1.01	2.35	8.09
6	80.09	7.43	0.43	1.03	2.61	8.41
Average Values	80.51 ± 3.78	7.33 ± 0.18	0.43 ± 0.08	1.05 ± 0.15	2.47 ± 1.64	8.21 ± 2.19

Table C.3: Dry ashing results

Analysis Number	Crumb Rubber			Tire Chips		
	Initial Weight (mg)	Final Weight (mg)	Ash Fraction (%)	Initial Weight (mg)	Final Weight (mg)	Ash Fraction (%)
1	788.9	48.0	6.08	4261.8	864.6	20.29
2	1003.6	73.3	7.30	1391.3	331.6	23.83
3	489.8	31.0	6.33	3903.4	710.8	18.21
4	428.3	28.8	6.72	1520.7	356.8	23.46
5	716.5	48.5	6.77	1961.4	370.8	18.90
Average Ash Fraction (%)	6.64 ± 0.66			20.94 ± 2.89		

Appendix D

Table D.1: Experimental data for crumb rubber in pH 4.0 solution

Time (Days)	pH	UV_{254}	DOC Concentrations (mg/L)	Cumulative DOC Masses (mg/100g)	DOC (M/M_{Max}) (%)	DN Concentrations (mg/L)	Cumulative DN Masses (mg/100g)	DN (M/M_{Max}) (%)
1	6.06	0.1947	10.99	21.99	50.48	1.59	3.19	56.76
3	5.79	0.2132	12.17	24.34	55.88	1.72	3.43	61.08
5	5.73	0.2158	12.42	24.84	57.02	1.71	3.42	60.87
7	5.47	0.2097	12.42	24.85	57.04	1.77	3.54	63.05
8	5.88	0.0921	2.28	29.41	67.52	0.20	3.94	70.20
10	5.82	0.1042	3.31	31.46	72.22	0.31	4.16	74.08
12	5.73	0.1103	3.85	32.54	74.70	0.40	4.34	77.26
14	4.90	0.1114	4.09	33.02	75.81	0.47	4.49	79.87
15	5.39	0.0716	2.02	37.06	85.07	0.21	4.91	87.34
17	5.32	0.0803	2.35	37.72	86.58	0.25	4.99	88.87
19	4.70	0.0849	2.57	38.16	87.61	0.27	5.03	89.50
21	4.80	0.0885	3.00	39.03	89.59	0.32	5.12	91.09
22	4.45	0.0616	0.88	40.78	93.61	0.13	5.37	95.58
25	5.12	0.0697	1.75	42.52	97.62	0.18	5.49	97.67
28	4.89	0.0754	2.27	43.56	100.00	0.28	5.62	100.00

Table D.2: Experimental data for tire chips 1"×1" in pH 4.0 solution

Time (Days)	pH	UV_{254}	DOC Concentrations (mg/L)	Cumulative DOC Masses (mg/100g)	DOC (M/M_{Max}) (%)	DN Concentrations (mg/L)	Cumulative DN Masses (mg/100g)	DN (M/M_{Max}) (%)
1	4.73	0.0696	3.09	6.18	31.79	0.46	0.92	30.82
3	5.01	0.0905	4.05	8.10	41.67	0.60	1.21	40.53
5	4.89	0.0989	4.26	8.51	43.82	0.65	1.31	43.92
7	5.00	0.1014	4.48	8.96	46.11	0.69	1.38	46.31
8	5.36	0.0374	0.75	1.49	53.78	0.12	1.62	54.47
10	5.00	0.0513	1.48	2.95	61.30	0.20	1.78	59.59
12	4.97	0.0597	1.81	3.62	64.73	0.26	1.89	63.55
14	4.89	0.0666	2.12	4.25	67.97	0.31	2.01	67.37
15	5.31	0.0236	0.52	1.04	73.33	0.11	2.22	74.65
17	5.04	0.0372	0.95	1.90	77.77	0.18	2.37	79.41
19	4.85	0.0499	1.23	2.46	80.63	0.21	2.42	81.19
21	4.77	0.0579	1.65	3.31	85.01	0.27	2.55	85.51
22	5.38	0.0218	0.50	1.01	90.20	<MRL	NA	NA
25	5.07	0.0358	1.00	2.00	95.30	0.13	2.81	94.33
28	4.80	0.0483	1.46	2.91	100.00	0.22	2.98	100.00

<MRL: Concentration below minimum reporting level.
NA: Not Applicable.

Table D.3: Experimental data for tire chips 2"×2" in pH 4.0 solution

Time (Days)	pH	UV_{254}	DOC Concentrations (mg/L)	Cumulative DOC Masses (mg/100g)	DOC (M/M_{Max}) (%)	DN Concentrations (mg/L)	Cumulative DN Masses (mg/100g)	DN (M/M_{Max}) (%)
1	4.16	0.0489	2.28	4.57	36.13	0.41	0.81	45.28
3	4.56	0.0582	2.93	5.86	46.34	0.61	1.22	68.01
5	4.65	0.0579	2.82	5.64	44.58	0.54	1.08	60.08
7	4.79	0.0614	2.89	5.78	45.74	0.51	1.02	56.80
8	2.67	0.0155	0.37	6.53	51.66	0.08	1.18	65.69
10	4.54	0.0263	0.85	7.48	59.14	0.15	1.32	73.23
12	4.51	0.0326	1.01	7.80	61.64	0.17	1.36	75.53
14	4.11	0.0369	1.40	8.58	67.88	0.20	1.42	79.08
15	4.35	0.0128	0.41	9.39	74.29	<MRL	NA	NA
17	4.30	0.0196	0.56	9.71	76.75	<MRL	NA	NA
19	4.46	0.0253	0.78	10.14	80.18	0.11	1.64	90.88
21	4.06	0.0325	1.08	10.75	85.02	0.15	1.73	96.13
22	4.35	0.0120	0.44	11.63	91.95	<MRL	NA	NA
25	4.78	0.0190	0.74	12.22	96.66	<MRL	NA	NA
28	4.62	0.0270	0.95	12.65	100.00	0.10	1.80	100.00

<MRL: Concentration below minimum reporting level.
NA: Not Applicable.

Table D.4: Experimental data for tire chips 4"×2" in pH 4.0 solution

Time (Days)	pH	UV_{254}	DOC Concentrations (mg/L)	Cumulative DOC Masses (mg/100g)	DOC (M/M_{Max}) (%)	DN Concentrations (mg/L)	Cumulative DN Masses (mg/100g)	DN (M/M_{Max}) (%)
1	4.39	0.0551	1.83	3.66	39.69	0.22	0.44	31.95
3	4.75	0.0662	2.04	4.08	44.31	0.25	0.50	36.73
5	4.72	0.0682	2.18	4.36	47.29	0.28	0.55	40.39
7	4.90	0.0693	2.23	4.46	48.38	0.31	0.62	45.19
8	4.51	0.0290	0.40	0.79	57.00	<MRL	NA	NA
10	5.06	0.0358	0.64	1.28	62.30	0.10	0.82	60.15
12	4.96	0.0417	0.80	1.60	65.74	0.12	0.87	63.36
14	4.80	0.0474	0.91	1.82	68.17	0.14	0.91	66.28
15	4.51	0.0238	0.32	0.63	75.01	<MRL	NA	NA
17	4.89	0.0298	0.47	0.95	78.46	<MRL	NA	NA
19	4.65	0.0374	0.64	1.27	82.00	0.11	1.13	82.22
21	4.62	0.0430	0.74	1.47	84.16	0.12	1.14	83.20
22	4.51	0.0238	0.37	0.75	92.27	<MRL	NA	NA
25	5.18	0.0288	0.61	1.23	97.47	<MRL	NA	NA
28	4.88	0.0367	0.73	1.46	100.00	0.12	1.37	100.00

<MRL: Concentration below minimum reporting level.
NA: Not Applicable.

Table D.5: Experimental data for tire chips 6"×2" in pH 4.0 solution

Time (Days)	pH	UV_{254}	DOC Concentrations (mg/L)	Cumulative DOC Masses (mg/100g)	DOC (M/M_{Max}) (%)	DN Concentrations (mg/L)	Cumulative DN Masses (mg/100g)	DN (M/M_{Max}) (%)
1	4.37	0.0590	1.78	3.55	37.74	0.22	0.43	32.53
3	4.52	0.0665	1.86	3.72	39.49	0.23	0.47	35.34
5	4.29	0.0753	2.18	4.36	46.32	0.27	0.54	40.64
7	4.65	0.0789	2.22	4.44	47.15	0.28	0.57	42.76
8	4.26	0.0393	0.44	5.33	56.58	<MRL	NA	NA
10	4.95	0.0449	0.67	5.77	61.34	<MRL	NA	NA
12	4.73	0.0515	0.90	6.24	66.28	0.11	0.79	59.55
14	4.46	0.0581	1.18	6.80	72.25	0.16	0.89	67.28
15	4.62	0.0370	0.59	7.98	84.75	<MRL	NA	NA
17	4.93	0.0423	0.58	7.96	84.58	<MRL	NA	NA
19	4.50	0.0503	0.84	8.48	90.11	0.10	1.09	82.08
21	4.66	0.0523	0.58	7.97	84.63	0.10	1.09	82.31
22	4.30	0.0349	0.35	8.67	92.10	<MRL	NA	NA
25	4.94	0.0421	0.54	9.04	96.00	<MRL	NA	NA
28	4.53	0.0472	0.72	9.41	100.00	0.12	1.33	100.00

<MRL: Concentration below minimum reporting level.
NA: Not Applicable.

Table D.6: Experimental data for crumb rubber in pH 7.0 solution

Time (Days)	pH	UV_{254}	DOC Concentrations (mg/L)	Cumulative DOC Masses (mg/100g)	DOC (M/M_{Max}) (%)	DN Concentrations (mg/L)	Cumulative DN Masses (mg/100g)	DN (M/M_{Max}) (%)
1	7.04	0.2083	13.48	26.95	47.86	1.45	2.90	49.25
3	6.90	0.2394	15.82	31.64	56.18	1.69	3.37	57.31
5	6.68	0.2313	15.65	31.31	55.59	1.71	3.42	58.18
7	6.67	0.2291	15.75	31.51	55.95	1.73	3.46	58.90
8	7.02	0.0696	3.03	37.56	66.69	0.24	3.94	67.00
10	7.11	0.0822	4.10	39.72	70.52	0.36	4.19	71.31
12	6.93	0.0878	4.85	41.21	73.18	0.46	4.38	74.43
14	6.90	0.0934	5.44	42.39	75.28	0.52	4.50	76.49
15	6.85	0.0498	2.04	46.48	82.53	0.18	4.86	82.68
17	6.78	0.0564	2.85	48.09	85.39	0.29	5.07	86.25
19	6.70	0.0618	3.27	48.94	86.90	0.33	5.16	87.73
21	6.67	0.0694	3.91	50.21	89.17	0.39	5.29	89.86
22	6.64	0.0379	1.64	53.49	94.98	0.15	5.58	94.85
25	6.70	0.0449	2.35	54.92	97.52	0.22	5.72	97.25
28	6.54	0.0517	3.05	56.32	100.00	0.30	5.88	100.00

Table D.7: Experimental data for tire chips 1"×1" in pH 7.0 solution

Time (Days)	pH	UV_{254}	DOC Concentrations (mg/L)	Cumulative DOC Masses (mg/100g)	DOC (M/M_{Max}) (%)	DN Concentrations (mg/L)	Cumulative DN Masses (mg/100g)	DN (M/M_{Max}) (%)
1	6.87	0.0539	2.57	5.14	26.27	0.44	0.88	29.58
3	6.94	0.0693	3.51	7.02	35.87	0.56	1.13	38.04
5	6.75	0.0797	3.85	7.69	39.32	0.58	1.16	39.28
7	6.79	0.0846	4.11	8.22	42.02	0.64	1.28	43.26
8	6.36	0.0256	0.76	1.52	49.79	0.11	1.51	51.01
10	6.60	0.0368	1.42	2.84	56.54	0.18	1.63	55.20
12	6.64	0.0509	1.86	3.73	61.08	0.25	1.78	60.27
14	6.60	0.0579	2.20	4.41	64.56	0.30	1.89	63.83
15	6.08	0.0235	0.67	1.34	71.40	0.11	2.11	71.40
17	6.47	0.0346	1.18	2.36	76.63	0.19	2.27	76.77
19	6.55	0.0450	1.52	3.05	80.13	0.22	2.34	78.91
21	6.54	0.0489	1.89	3.79	83.92	0.30	2.50	84.29
22	6.46	0.0200	0.55	1.10	89.54	<MRL	NA	NA
25	6.95	0.0345	1.07	2.14	94.84	0.15	2.79	94.30
28	6.70	0.0425	1.57	3.14	100.00	0.23	2.96	100.00

<MRL: Concentration below minimum reporting level.
NA: Not Applicable.

Table D.8: Experimental data for tire chips 2"×2" in pH 7.0 solution

Time (Days)	pH	UV_{254}	DOC Concentrations (mg/L)	Cumulative DOC Masses (mg/100g)	DOC (M/M_{Max}) (%)	DN Concentrations (mg/L)	Cumulative DN Masses (mg/100g)	DN (M/M_{Max}) (%)
1	6.77	0.0798	2.81	5.61	43.31	0.26	0.52	42.27
3	6.40	0.1110	3.12	6.23	48.10	0.26	0.51	41.67
5	6.42	0.1183	3.30	6.60	50.95	0.28	0.56	45.60
7	6.46	0.1264	3.34	6.68	51.51	0.28	0.57	45.90
8	6.33	0.0243	0.59	7.87	60.69	<MRL	NA	NA
10	6.82	0.0316	0.81	8.29	64.00	<MRL	NA	NA
12	6.49	0.0332	1.18	9.04	69.74	0.12	0.80	65.19
14	6.47	0.0373	1.35	9.38	72.39	0.12	0.81	66.06
15	6.19	0.0168	0.47	10.31	79.59	<MRL	NA	NA
17	6.58	0.0258	0.75	10.88	83.93	0.10	1.01	81.78
19	6.61	0.0265	0.81	10.99	84.82	0.10	1.02	82.81
21	6.44	0.0299	1.00	11.38	87.80	0.11	1.03	83.80
22	6.36	0.0157	0.43	12.24	94.44	<MRL	NA	NA
25	6.74	0.0236	0.64	12.65	97.60	<MRL	NA	NA
28	6.69	0.0264	0.79	12.96	100.00	0.10	1.23	100.00

<MRL: Concentration below minimum reporting level.
NA: Not Applicable.

Table D.9: Experimental data for tire chips 4"×2" in pH 7.0 solution

Time (Days)	pH	UV_{254}	DOC Concentrations (mg/L)	Cumulative DOC Masses (mg/100g)	DOC (M/M_{Max}) (%)	DN Concentrations (mg/L)	Cumulative DN Masses (mg/100g)	DN (M/M_{Max}) (%)
1	6.88	0.0451	2.06	4.12	37.68	0.41	0.81	30.28
3	7.12	0.0608	2.50	5.01	45.86	0.52	1.04	38.96
5	6.83	0.0550	2.27	4.53	41.47	0.44	0.88	32.74
7	6.85	0.0581	2.42	4.84	44.28	0.49	0.98	36.65
8	6.59	0.0102	0.44	5.72	52.35	<MRL	NA	NA
10	6.48	0.0178	0.68	6.21	56.81	<MRL	NA	NA
12	6.64	0.0248	0.88	6.60	60.41	0.12	1.22	45.55
14	6.62	0.0315	1.21	7.26	66.41	0.18	1.35	50.20
15	6.14	0.0081	0.37	7.99	73.10	0.12	1.59	59.30
17	6.52	0.0143	0.57	8.39	76.84	0.31	1.96	73.19
19	6.53	0.0207	0.76	8.77	80.27	0.38	2.11	78.77
21	6.66	0.0260	1.07	9.39	85.92	0.55	2.44	90.99
22	6.42	0.0082	0.33	10.05	92.02	<MRL	NA	NA
25	6.75	0.0167	0.58	10.54	96.46	<MRL	NA	NA
28	6.73	0.0210	0.77	10.92	100.00	0.12	2.68	100.00

<MRL: Concentration below minimum reporting level.
NA: Not Applicable.

Table D.10: Experimental data for tire chips 6"×2" in pH 7.0 solution

Time (Days)	pH	UV_{254}	DOC Concentrations (mg/L)	Cumulative DOC Masses (mg/100g)	DOC (M/M_{Max}) (%)	DN Concentrations (mg/L)	Cumulative DN Masses (mg/100g)	DN (M/M_{Max}) (%)
1	6.81	0.0506	1.84	3.68	31.01	0.26	0.53	32.16
3	6.26	0.0645	2.29	4.58	38.53	0.29	0.59	35.92
5	6.53	0.0667	2.55	5.09	42.90	0.34	0.68	41.55
7	6.36	0.0755	2.63	5.25	44.23	0.34	0.68	41.58
8	6.76	0.0260	0.55	6.35	53.44	<MRL	NA	NA
10	6.85	0.0319	0.88	7.02	59.07	0.12	0.92	56.02
12	6.45	0.0396	1.10	7.45	62.71	0.14	0.95	58.06
14	6.32	0.0425	1.29	7.84	66.02	0.18	1.04	63.25
15	6.33	0.0248	0.50	8.84	74.46	<MRL	NA	NA
17	6.92	0.0282	0.86	9.56	80.53	0.11	1.27	77.15
19	6.75	0.0326	0.86	9.57	80.56	0.13	1.30	79.15
21	6.22	0.0384	1.08	9.99	84.16	0.17	1.37	83.53
22	6.70	0.0207	0.45	10.90	91.78	<MRL	NA	NA
25	6.40	0.0275	0.70	11.39	95.95	0.12	1.61	97.86
28	6.82	0.0321	0.94	11.88	100.00	0.14	1.64	100.00

<MRL: Concentration below minimum reporting level.
NA: Not Applicable.

Table D.11: Experimental data for crumb rubber in pH 10.0 solution

Time (Days)	pH	UV_{254}	DOC Concentrations (mg/L)	Cumulative DOC Masses (mg/100g)	DOC (M/M_{Max}) (%)	DN Concentrations (mg/L)	Cumulative DN Masses (mg/100g)	DN (M/M_{Max}) (%)
1	9.54	0.2857	18.42	36.85	30.13	1.47	2.93	57.36
3	9.70	0.3844	23.58	47.15	38.56	1.64	3.28	64.14
5	8.95	0.3885	26.21	52.43	42.87	1.33	2.67	52.10
7	9.49	0.4332	30.58	61.15	50.01	1.39	2.78	54.39
8	8.95	0.1187	6.08	73.30	59.94	0.30	3.37	65.93
10	9.34	0.1422	9.76	80.68	65.98	0.37	3.53	69.04
12	9.38	0.1604	12.36	85.87	70.23	0.46	3.71	72.48
14	9.32	0.1749	14.24	89.64	73.30	0.54	3.87	75.62
15	9.30	0.0687	4.81	99.26	81.17	0.20	4.26	83.30
17	9.49	0.0892	6.56	102.75	84.03	0.25	4.37	85.34
19	9.00	0.0981	7.66	104.95	85.83	0.31	4.49	87.84
21	9.55	0.0719	10.38	110.39	90.28	0.40	4.67	91.30
22	9.55	0.0553	3.10	116.59	95.34	0.10	4.87	95.26
25	9.59	0.0732	5.99	122.38	100.08	0.18	5.03	98.36
28	8.93	0.0728	5.94	122.28	100.00	0.22	5.12	100.00

Table D.12: Experimental data for tire chips 1"×1" in pH 10.0 solution

Time (Days)	pH	UV_{254}	DOC Concentrations (mg/L)	Cumulative DOC Masses (mg/100g)	DOC (M/M_{Max}) (%)	DN Concentrations (mg/L)	Cumulative DN Masses (mg/100g)	DN (M/M_{Max}) (%)
1	9.80	0.0746	3.10	6.20	22.94	0.45	0.90	33.81
3	9.92	0.1116	5.23	10.46	38.70	0.59	1.17	43.91
5	9.74	0.1111	6.06	12.12	44.84	0.53	1.07	39.93
7	10.09	0.1335	6.64	13.29	49.15	0.61	1.22	45.80
8	9.87	0.0230	0.82	1.63	55.19	0.15	1.52	56.82
10	9.91	0.0382	1.89	3.77	63.11	0.22	1.66	62.21
12	9.90	0.0522	2.52	5.04	67.80	0.27	1.77	66.05
14	9.80	0.0613	3.06	6.13	71.82	0.29	1.81	67.63
15	9.93	0.0181	0.73	1.47	77.24	0.13	2.08	77.67
17	9.95	0.0309	1.34	2.68	81.72	0.19	2.18	81.66
19	9.76	0.0423	1.82	3.64	85.29	0.23	2.26	84.64
21	9.95	0.0460	2.12	4.24	87.51	0.24	2.29	85.53
22	10.01	0.0217	0.59	1.19	91.90	0.12	2.52	94.16
25	9.96	0.0309	1.15	2.31	96.05	0.15	2.60	97.10
28	9.82	0.0492	1.69	3.38	100.00	0.19	2.67	100.00

Table D.13: Experimental data for tire chips 2"×2" in pH 10.0 solution

Time (Days)	pH	UV_{254}	DOC Concentrations (mg/L)	Cumulative DOC Masses (mg/100g)	DOC (M/M_{Max}) (%)	DN Concentrations (mg/L)	Cumulative DN Masses (mg/100g)	DN (M/M_{Max}) (%)
1	9.85	0.0722	3.68	7.36	26.95	0.39	0.78	39.34
3	9.60	0.1076	5.73	11.45	41.93	0.40	0.81	40.93
5	9.80	0.1206	6.29	12.58	46.05	0.41	0.81	41.16
7	9.90	0.1316	6.58	13.16	48.17	0.44	0.87	44.19
8	9.86	0.0133	0.98	15.13	55.37	0.10	1.07	54.22
10	9.82	0.0260	1.94	17.04	62.40	0.14	1.15	58.32
12	9.87	0.0406	2.65	18.46	67.59	0.19	1.26	63.90
14	9.92	0.0527	3.14	19.44	71.18	0.22	1.32	66.85
15	9.92	0.0083	0.80	21.05	77.07	<MRL	NA	NA
17	10.03	0.0176	1.52	22.48	82.31	0.12	1.56	79.10
19	9.66	0.0267	1.97	23.39	85.62	0.18	1.68	85.31
21	9.90	0.0373	2.32	24.08	88.17	0.19	1.70	86.44
22	9.99	0.0035	0.61	25.30	92.61	<MRL	NA	NA
25	10.00	0.0147	0.89	25.86	94.68	<MRL	NA	NA
28	9.71	0.0209	1.62	27.31	100.00	0.13	1.97	100.00

<MRL: Concentration below minimum reporting level.
NA: Not Applicable.

Table D.14: Experimental data for tire chips 4"×2" in pH 10.0 solution

Time (Days)	pH	UV_{254}	DOC Concentrations (mg/L)	Cumulative DOC Masses (mg/100g)	DOC (M/M_{Max}) (%)	DN Concentrations (mg/L)	Cumulative DN Masses (mg/100g)	DN (M/M_{Max}) (%)
1	9.77	0.0716	3.39	6.78	29.39	0.38	0.76	29.84
3	10.12	0.1125	5.30	10.60	45.94	0.52	1.04	40.71
5	9.81	0.1237	5.49	10.98	47.58	0.34	0.67	26.45
7	10.08	0.1352	5.83	11.65	50.49	0.51	1.02	39.93
8	9.88	0.0136	0.57	1.13	55.39	<MRL	NA	NA
10	9.85	0.0288	1.20	2.39	60.86	0.14	1.30	51.20
12	9.95	0.0438	1.91	3.82	67.04	0.20	1.42	55.81
14	9.87	0.0520	2.33	4.66	70.67	0.22	1.45	57.00
15	9.94	0.0118	0.53	1.07	75.29	0.15	1.75	68.81
17	9.93	0.0214	0.97	1.94	79.07	0.26	1.97	77.45
19	9.76	0.0325	1.44	2.89	83.18	0.33	2.10	82.53
21	9.94	0.0410	1.85	3.71	86.74	0.37	2.20	86.23
22	10.17	0.0081	0.62	1.23	92.08	<MRL	NA	NA
25	10.00	0.0198	0.95	1.91	95.01	0.11	2.43	95.23
28	9.89	0.0299	1.53	3.06	100.00	0.18	2.55	100.00

<MRL: Concentration below minimum reporting level.
NA: Not Applicable.

Table D.15: Experimental data for tire chips 6"×2" in pH 10.0 solution

Time (Days)	pH	UV_{254}	DOC Concentrations (mg/L)	Cumulative DOC Masses (mg/100g)	DOC (M/M_{Max}) (%)	DN Concentrations (mg/L)	Cumulative DN Masses (mg/100g)	DN (M/M_{Max}) (%)
1	9.83	0.0613	3.24	6.48	34.70	0.34	0.67	46.19
3	9.92	0.0907	4.67	9.35	50.04	0.35	0.71	48.77
5	9.83	0.0897	4.74	9.47	50.70	0.34	0.67	46.19
7	10.05	0.0979	4.95	9.89	52.95	0.38	0.76	52.29
8	9.97	0.0122	0.67	11.24	60.14	<MRL	NA	NA
10	9.92	0.0143	1.20	12.28	65.75	0.12	1.01	69.17
12	9.87	0.0231	1.68	13.25	70.92	0.18	1.13	77.44
14	9.98	0.0272	1.90	13.69	73.30	0.15	1.05	72.35
15	10.00	0.0061	0.59	14.88	79.65	<MRL	NA	NA
17	9.97	0.0096	0.89	15.47	82.82	<MRL	NA	NA
19	9.68	0.0165	1.10	15.90	85.12	0.12	1.28	88.40
21	10.01	0.0199	1.63	16.95	90.71	0.12	1.29	88.83
22	10.03	0.0021	0.45	17.84	95.52	<MRL	NA	NA
25	9.92	0.0082	0.68	18.30	97.94	<MRL	NA	NA
28	9.86	0.0130	0.87	18.68	100.00	0.10	1.45	100.00

<MRL: Concentration below minimum reporting level.
NA: Not Applicable.

Table D.16: Experimental data for crumb rubber in rainwater (at pH 3.0)

Time (Days)	pH	UV_{254}	DOC Concentrations (mg/L)	Cumulative DOC Masses (mg/100g)	DOC (M/M_{Max}) (%)	DN Concentrations (mg/L)	Cumulative DN Masses (mg/100g)	DN (M/M_{Max}) (%)
1	4.29	0.1661	11.17	22.35	35.79	1.67	3.34	40.95
3	3.37	0.2069	13.07	26.14	41.88	2.08	4.16	50.90
5	3.23	0.2231	14.35	28.71	45.98	2.12	4.24	51.99
7	3.06	0.2344	15.60	31.20	49.98	2.26	4.51	55.25
8	3.11	0.0739	2.72	36.64	58.68	0.28	5.07	62.06
10	3.08	0.0955	4.04	39.28	62.92	0.45	5.41	66.31
12	3.07	0.1077	4.96	41.12	65.86	0.60	5.70	69.85
14	3.02	0.1201	5.82	42.85	68.63	0.71	5.92	72.52
15	3.02	0.0474	1.81	46.48	74.44	0.20	6.32	77.44
17	3.01	0.0725	2.89	48.64	77.90	0.33	6.57	80.50
19	3.05	0.0953	4.11	51.08	81.81	0.46	6.85	83.85
21	3.07	0.1182	5.24	53.34	85.43	0.60	7.12	87.20
22	3.07	0.0298	1.66	56.65	90.73	0.18	7.47	91.54
25	3.08	0.0472	3.02	59.37	95.09	0.34	7.80	95.54
28	3.04	0.0675	4.55	62.43	100.00	0.52	8.17	100.00

Table D.17: Experimental data for tire chips 1"×1" in rainwater (at pH 3.0)

Time (Days)	pH	UV_{254}	DOC Concentrations (mg/L)	Cumulative DOC Masses (mg/100g)	DOC (M/M_{Max}) (%)	DN Concentrations (mg/L)	Cumulative DN Masses (mg/100g)	DN (M/M_{Max}) (%)
1	3.81	0.1042	2.73	5.47	22.28	0.33	0.66	21.25
3	3.85	0.1440	4.30	8.59	34.99	0.45	0.91	29.16
5	3.83	0.1629	5.04	10.07	41.02	0.51	1.02	32.76
7	3.50	0.2001	5.46	10.91	44.46	0.59	1.17	37.56
8	3.54	0.0510	0.94	12.79	52.10	0.13	1.42	45.74
10	3.60	0.0815	1.78	14.47	58.95	0.24	1.64	52.68
12	3.38	0.1169	2.39	15.69	63.89	0.33	1.83	58.70
14	3.30	0.1377	2.82	16.56	67.47	0.40	1.96	62.98
15	3.01	0.0330	0.76	18.09	73.68	0.13	2.23	71.55
17	3.30	0.0925	1.29	19.15	78.02	0.19	2.35	75.45
19	3.26	0.1046	1.71	19.99	81.42	0.24	2.44	78.48
21	3.18	0.1271	2.10	20.76	84.57	0.30	2.57	82.55
22	3.36	0.0546	0.73	22.21	90.48	0.11	2.78	89.32
25	3.11	0.0656	1.33	23.43	95.45	0.18	2.94	94.41
28	3.19	0.1013	1.89	24.55	100.00	0.27	3.12	100.00

Table D.18: Experimental data for tire chips 2"×2" in rainwater (at pH 3.0)

Time (Days)	pH	UV_{254}	DOC Concentrations (mg/L)	Cumulative DOC Masses (mg/100g)	DOC (M/M_{Max}) (%)	DN Concentrations (mg/L)	Cumulative DN Masses (mg/100g)	DN (M/M_{Max}) (%)
1	3.36	0.1012	2.28	4.56	31.76	0.27	0.54	27.65
3	3.33	0.1366	2.97	5.94	41.32	0.36	0.72	36.82
5	3.32	0.1382	3.03	6.06	42.18	0.38	0.76	38.73
7	3.15	0.1731	3.19	6.37	44.34	0.44	0.88	44.58
8	3.20	0.0730	0.68	7.74	53.84	<MRL	NA	NA
10	3.17	0.1077	1.14	8.66	60.23	0.14	1.16	59.00
12	3.12	0.1249	1.41	9.19	63.94	0.18	1.24	63.14
14	3.07	0.1272	1.59	9.56	66.53	0.21	1.30	65.95
15	2.99	0.0353	0.49	10.54	73.32	<MRL	NA	NA
17	3.07	0.1010	0.76	11.08	77.12	<MRL	NA	NA
19	3.04	0.1268	1.02	11.60	80.69	0.14	1.57	79.90
21	3.04	0.1212	1.19	11.93	83.03	0.16	1.62	82.34
22	3.14	0.0619	0.54	13.01	90.55	0.10	1.81	92.31
25	3.08	0.0944	0.91	13.76	95.71	0.14	1.90	96.88
28	3.04	0.1326	1.22	14.37	100.00	0.17	1.96	100.00

<MRL: Concentration below minimum reporting level.
NA: Not Applicable.

Table D.19: Experimental data for tire chips 4"×2" in rainwater (at pH 3.0)

Time (Days)	pH	UV_{254}	DOC Concentrations (mg/L)	Cumulative DOC Masses (mg/100g)	DOC (M/M_{Max}) (%)	DN Concentrations (mg/L)	Cumulative DN Masses (mg/100g)	DN (M/M_{Max}) (%)
1	3.36	0.0906	1.74	3.49	29.62	0.23	0.45	25.72
3	3.26	0.1200	2.36	4.73	40.11	0.30	0.61	34.44
5	3.23	0.1401	2.54	5.08	43.08	0.34	0.68	38.72
7	3.17	0.1589	2.66	5.32	45.16	0.38	0.77	43.43
8	3.20	0.0931	0.67	6.65	56.46	<MRL	NA	NA
10	3.13	0.1220	1.03	7.37	62.56	0.14	1.04	58.83
12	3.11	0.1274	1.23	7.78	66.06	0.16	1.09	61.85
14	3.05	0.1305	1.35	8.03	68.13	0.18	1.13	64.06
15	3.03	0.0448	0.42	8.86	75.23	<MRL	NA	NA
17	3.08	0.1337	0.68	9.38	79.66	0.10	1.33	75.54
19	3.05	0.1490	0.81	9.65	81.93	0.12	1.37	77.64
21	3.03	0.1533	0.96	9.96	84.50	0.15	1.42	80.57
22	3.17	0.0990	0.44	10.83	91.94	<MRL	NA	NA
25	3.06	0.1234	0.76	11.47	97.39	0.13	1.69	95.64
28	3.05	0.1505	0.91	11.78	100.00	0.17	1.76	100.00

<MRL: Concentration below minimum reporting level.
NA: Not Applicable.

Table D.20: Experimental data for tire chips 6"×2" in rainwater (at pH 3.0)

Time (Days)	pH	UV_{254}	DOC Concentrations (mg/L)	Cumulative DOC Masses (mg/100g)	DOC (M/M_{Max}) (%)	DN Concentrations (mg/L)	Cumulative DN Masses (mg/100g)	DN (M/M_{Max}) (%)
1	3.75	0.0703	2.04	4.09	32.42	0.22	0.44	27.41
3	3.69	0.0846	2.48	4.96	39.34	0.28	0.55	34.80
5	3.59	0.1041	2.57	5.15	40.84	0.31	0.61	38.59
7	3.33	0.1312	2.78	5.57	44.18	0.34	0.67	42.19
8	3.49	0.0443	0.59	6.76	53.60	<MRL	NA	NA
10	3.34	0.0789	1.46	8.48	67.26	0.25	1.16	73.00
12	3.22	0.0893	1.20	7.96	63.16	0.14	0.94	59.26
14	3.12	0.1074	1.43	8.44	66.93	0.19	1.05	65.93
15	3.03	0.0207	0.41	9.26	73.48	<MRL	NA	NA
17	3.09	0.0758	0.66	9.76	77.44	<MRL	NA	NA
19	3.13	0.0891	0.88	10.19	80.84	0.10	1.26	78.94
21	3.08	0.1044	1.03	10.49	83.21	0.13	1.31	82.01
22	3.17	0.0520	0.49	11.46	90.92	<MRL	NA	NA
25	3.11	0.0713	0.84	12.17	96.52	0.13	1.57	98.52
28	3.06	0.1191	1.06	12.61	100.00	0.14	1.59	100.00

<MRL: Concentration below minimum reporting level.
NA: Not Applicable.

Table D.21: Experimental data for crumb rubber in soft groundwater (at pH 6.3)

Time (Days)	pH	UV_{254}	DOC Concentrations (mg/L)	Cumulative DOC Masses (mg/100g)	DOC (M/M_{Max}) (%)	DN Concentrations (mg/L)	Cumulative DN Masses (mg/100g)	DN (M/M_{Max}) (%)
1	6.93	0.1597	12.36	24.71	50.22	1.48	2.97	50.95
3	6.74	0.1804	12.97	25.94	52.72	1.51	3.02	51.79
5	6.51	0.1797	13.18	26.36	53.57	1.63	3.26	55.94
7	6.52	0.1854	13.25	26.51	53.87	1.66	3.33	57.14
8	6.76	0.0600	2.72	31.96	64.94	0.26	3.85	66.05
10	6.66	0.0732	3.77	34.04	69.17	0.39	4.10	70.36
12	6.46	0.0791	4.41	35.32	71.78	0.49	4.31	74.04
14	6.16	0.0833	4.99	36.50	74.17	0.57	4.46	76.60
15	6.57	0.0422	1.87	40.23	81.75	0.20	4.86	83.35
17	6.58	0.0504	2.56	41.62	84.58	0.27	4.99	85.73
19	6.52	0.0560	3.15	42.79	86.96	0.33	5.13	88.00
21	6.31	0.0597	3.48	43.46	88.31	0.38	5.22	89.64
22	6.65	0.0312	1.39	46.23	93.94	0.11	5.44	93.38
25	6.24	0.0367	1.92	47.29	96.10	0.17	5.57	95.54
28	6.35	0.0470	2.88	49.21	100.00	0.30	5.83	100.00

<MRL: Concentration below minimum reporting level.
NA: Not Applicable.

Table D.22: Experimental data for tire chips 1"×1" in soft groundwater (at pH 6.3)

Time (Days)	pH	UV_{254}	DOC Concentrations (mg/L)	Cumulative DOC Masses (mg/100g)	DOC (M/M_{Max}) (%)	DN Concentrations (mg/L)	Cumulative DN Masses (mg/100g)	DN (M/M_{Max}) (%)
1	6.33	0.0406	2.25	4.50	25.05	0.30	0.61	25.03
3	6.35	0.0564	3.17	6.33	35.28	0.44	0.87	35.89
5	5.94	0.0743	3.61	7.21	40.19	0.50	1.01	41.42
7	6.30	0.0773	3.93	7.87	43.83	0.55	1.09	44.93
8	6.69	0.0159	0.77	9.40	52.38	0.13	1.35	55.42
10	6.32	0.0320	1.43	10.72	59.74	0.19	1.48	60.89
12	6.27	0.0389	1.84	11.55	64.35	0.25	1.59	65.25
14	6.07	0.0478	2.20	12.27	68.34	0.30	1.68	69.28
15	6.49	0.0164	0.71	13.68	76.21	0.12	1.92	78.96
17	6.45	0.0242	1.03	14.33	79.86	0.18	2.04	83.72
19	6.40	0.0327	1.42	15.10	84.13	0.21	2.11	86.87
21	6.15	0.0390	1.71	15.69	87.43	0.24	2.17	89.19
22	6.64	0.0155	0.55	16.78	93.52	<MRL	NA	NA
25	6.04	0.0269	0.82	17.33	96.55	<MRL	NA	NA
28	6.34	0.0327	1.13	17.95	100.00	0.13	2.43	100.00

<MRL: Concentration below minimum reporting level.
NA: Not Applicable.

Table D.23: Experimental data for tire chips 2"×2" in soft groundwater (at pH 6.3)

Time (Days)	pH	UV_{254}	DOC Concentrations (mg/L)	Cumulative DOC Masses (mg/100g)	DOC (M/M_{Max}) (%)	DN Concentrations (mg/L)	Cumulative DN Masses (mg/100g)	DN (M/M_{Max}) (%)
1	6.33	0.0453	1.81	3.62	33.26	0.17	0.35	27.76
3	6.37	0.0360	1.95	3.89	35.80	0.17	0.34	27.04
5	6.17	0.0389	2.12	4.24	38.97	0.19	0.39	30.97
7	6.27	0.0424	2.30	4.59	42.26	0.22	0.44	35.56
8	6.56	0.0085	0.55	5.68	52.29	0.10	0.65	52.22
10	6.34	0.0152	0.87	6.32	58.18	0.13	0.70	56.13
12	6.30	0.0191	1.12	6.83	62.85	0.16	0.76	60.92
14	6.08	0.0232	1.38	7.36	67.73	0.19	0.83	66.58
15	6.45	0.0107	0.50	8.36	76.93	<MRL	NA	NA
17	6.38	0.0117	0.67	8.70	79.98	0.10	1.03	82.76
19	6.36	0.0173	0.85	9.06	83.35	0.13	1.09	87.66
21	6.13	0.0184	1.02	9.40	86.43	0.16	1.14	91.95
22	6.76	0.0096	0.35	10.09	92.83	<MRL	NA	NA
25	6.04	0.0124	0.49	10.38	95.50	<MRL	NA	NA
28	6.22	0.0144	0.74	10.87	100.00	0.10	1.24	100.00

<MRL: Concentration below minimum reporting level.
NA: Not Applicable.

Table D.24: Experimental data for tire chips 4"×2" in soft groundwater (at pH 6.3)

Time (Days)	pH	UV_{254}	DOC Concentrations (mg/L)	Cumulative DOC Masses (mg/100g)	DOC (M/M_{Max}) (%)	DN Concentrations (mg/L)	Cumulative DN Masses (mg/100g)	DN (M/M_{Max}) (%)
1	6.37	0.0798	3.26	6.53	39.34	0.33	0.66	42.21
3	6.21	0.0798	3.78	7.56	45.57	0.35	0.70	44.70
5	6.18	0.0850	4.11	8.23	49.59	0.37	0.73	46.74
7	6.40	0.0880	4.20	8.39	50.57	0.36	0.72	46.01
8	6.62	0.0170	0.72	9.83	59.23	0.11	0.95	60.19
10	6.22	0.0262	1.16	10.70	64.50	0.15	1.02	65.25
12	6.31	0.0337	1.73	11.85	71.43	0.18	1.09	69.32
14	6.10	0.0399	2.07	12.54	75.56	0.20	1.13	71.95
15	6.41	0.0135	0.55	13.64	82.22	0.10	1.33	84.75
17	6.37	0.0205	0.84	14.22	85.69	0.13	1.38	87.94
19	6.33	0.0254	1.12	14.78	89.06	0.14	1.41	89.64
21	6.16	0.0278	1.17	14.87	89.63	0.15	1.42	90.72
22	6.62	0.0134	0.38	15.63	94.22	<MRL	NA	NA
25	6.11	0.0178	0.64	16.14	97.29	<MRL	NA	NA
28	6.17	0.0233	0.86	16.59	100.00	0.10	1.57	100.00

<MRL: Concentration below minimum reporting level.
NA: Not Applicable.

Table D.25: Experimental data for tire chips 6"×2" in soft groundwater (at pH 6.3)

Time (Days)	pH	UV_{254}	DOC Concentrations (mg/L)	Cumulative DOC Masses (mg/100g)	DOC (M/M_{Max}) (%)	DN Concentrations (mg/L)	Cumulative DN Masses (mg/100g)	DN (M/M_{Max}) (%)
1	6.39	0.0682	2.65	5.29	33.34	0.27	0.55	28.01
3	6.33	0.0527	3.03	6.07	38.22	0.31	0.62	32.05
5	6.23	0.0560	3.36	6.72	42.36	0.36	0.72	36.96
7	6.38	0.0598	3.56	7.13	44.90	0.38	0.76	38.78
8	6.64	0.0168	0.70	8.52	53.68	0.15	1.05	53.75
10	6.37	0.0241	1.17	9.47	59.66	0.19	1.13	57.80
12	6.39	0.0258	1.55	10.22	64.40	0.21	1.17	59.91
14	6.03	0.0323	1.98	11.09	69.84	0.28	1.31	67.17
15	6.45	0.0120	0.59	12.27	77.29	0.11	1.52	78.15
17	6.34	0.0174	0.91	12.91	81.31	0.14	1.60	81.97
19	6.41	0.0207	1.11	13.30	83.80	0.17	1.64	84.18
21	6.22	0.0248	1.35	13.78	86.79	0.19	1.69	86.75
22	6.65	0.0096	0.45	14.67	92.41	<MRL	NA	NA
25	6.16	0.0158	0.78	15.34	96.62	<MRL	NA	NA
28	6.24	0.0216	1.05	15.88	100.00	0.13	1.95	100.00

<MRL: Concentration below minimum reporting level.
NA: Not Applicable.

Table D.26: Experimental data for crumb rubber in hard groundwater (at pH 8.1)

Time (Days)	pH	UV_{254}	DOC Concentrations (mg/L)	Cumulative DOC Masses (mg/100g)	DOC (M/M_{Max}) (%)	DN Concentrations (mg/L)	Cumulative DN Masses (mg/100g)	DN (M/M_{Max}) (%)
1	7.53	0.1674	11.88	23.76	38.80	1.39	2.79	56.62
3	7.76	0.2076	14.77	29.54	48.23	1.61	3.23	65.55
5	7.56	0.2241	15.93	31.87	52.03	1.37	2.74	55.76
7	7.58	0.2296	16.81	33.63	54.90	1.42	2.84	57.80
8	7.80	0.0664	3.46	40.54	66.19	0.22	3.28	66.72
10	7.38	0.0804	4.80	43.23	70.58	0.32	3.48	70.75
12	7.41	0.0934	5.69	45.01	73.49	0.44	3.72	75.55
14	7.42	0.1032	6.19	46.01	75.12	0.48	3.80	77.19
15	7.71	0.0441	2.50	51.01	83.28	0.12	4.04	82.14
17	7.79	0.0553	3.23	52.48	85.68	0.19	4.17	84.77
19	7.71	0.0596	3.78	53.57	87.46	0.23	4.26	86.63
21	7.30	0.0677	4.29	54.59	89.14	0.31	4.41	89.66
22	8.03	0.0370	1.75	58.09	94.85	0.11	4.63	94.15
25	7.67	0.0443	2.60	59.79	97.62	0.19	4.79	97.28
28	7.69	0.0569	3.33	61.25	100.00	0.25	4.92	100.00

Table D.27: Experimental data for tire chips 1"×1" in hard groundwater (at pH 8.1)

Time (Days)	pH	UV_{254}	DOC Concentrations (mg/L)	Cumulative DOC Masses (mg/100g)	DOC (M/M_{Max}) (%)	DN Concentrations (mg/L)	Cumulative DN Masses (mg/100g)	DN (M/M_{Max}) (%)
1	7.54	0.0453	2.60	5.21	25.80	0.36	0.71	27.60
3	7.82	0.0692	3.47	6.94	34.36	0.45	0.90	35.05
5	7.71	0.0787	3.74	7.48	37.04	0.45	0.90	34.94
7	7.70	0.0859	4.04	8.08	40.04	0.53	1.07	41.37
8	8.00	0.0222	0.57	9.23	45.70	0.11	1.28	49.74
10	7.73	0.0342	1.29	10.66	52.83	0.15	1.37	53.02
12	7.60	0.0479	1.88	11.84	58.68	0.23	1.52	59.01
14	7.60	0.0567	2.49	13.05	64.67	0.27	1.60	62.15
15	7.98	0.0158	0.48	14.02	69.44	<MRL	NA	NA
17	8.00	0.0264	1.01	15.07	74.65	0.12	1.84	71.16
19	7.97	0.0335	1.39	15.83	78.41	0.16	1.92	74.28
21	7.76	0.0429	1.94	16.94	83.92	0.22	2.04	79.20
22	8.22	0.0110	0.38	17.69	87.65	<MRL	NA	NA
25	8.02	0.0289	1.14	19.21	95.18	0.16	2.37	91.68
28	8.01	0.0399	1.62	20.19	100.00	0.27	2.58	100.00

<MRL: Concentration below minimum reporting level.
NA: Not Applicable.

Table D.28: Experimental data for tire chips 2"×2" in hard groundwater (at pH 8.1)

Time (Days)	pH	UV_{254}	DOC Concentrations (mg/L)	Cumulative DOC Masses (mg/100g)	DOC (M/M_{Max}) (%)	DN Concentrations (mg/L)	Cumulative DN Masses (mg/100g)	DN (M/M_{Max}) (%)
1	7.66	0.0616	3.26	6.51	34.66	0.30	0.60	50.94
3	7.84	0.0806	3.80	7.60	40.47	0.25	0.50	42.48
5	7.77	0.0905	4.16	8.31	44.24	0.26	0.52	44.16
7	7.75	0.0999	4.42	8.84	47.04	0.26	0.52	43.99
8	8.09	0.0114	0.42	9.68	51.50	<MRL	NA	NA
10	7.86	0.0291	0.98	10.80	57.48	<MRL	NA	NA
12	7.73	0.0368	1.66	12.16	64.69	0.10	0.73	61.28
14	7.72	0.0456	2.10	13.04	69.42	0.12	0.76	64.48
15	8.04	0.0083	0.43	13.91	74.05	<MRL	NA	NA
17	8.08	0.0146	0.69	14.42	76.75	<MRL	NA	NA
19	8.05	0.0241	1.19	15.43	82.14	<MRL	NA	NA
21	7.92	0.0322	1.50	16.05	85.43	0.10	0.96	81.02
22	8.26	0.0070	0.28	16.61	88.39	<MRL	NA	NA
25	8.13	0.0200	0.72	17.49	93.09	<MRL	NA	NA
28	8.07	0.0295	1.37	18.79	100.00	0.11	1.19	100.00

<MRL: Concentration below minimum reporting level.
NA: Not Applicable.

Table D.29: Experimental data for tire chips 4"×2" in hard groundwater (at pH 8.1)

Time (Days)	pH	UV_{254}	DOC Concentrations (mg/L)	Cumulative DOC Masses (mg/100g)	DOC (M/M_{Max}) (%)	DN Concentrations (mg/L)	Cumulative DN Masses (mg/100g)	DN (M/M_{Max}) (%)
1	7.70	0.0306	1.65	3.29	30.39	0.17	0.35	31.51
3	7.96	0.0462	2.13	4.26	39.27	0.17	0.33	29.96
5	7.90	0.0556	2.41	4.82	44.51	0.17	0.34	30.75
7	7.87	0.0620	2.57	5.15	47.51	0.23	0.46	42.01
8	8.10	0.0089	0.33	5.80	53.50	<MRL	NA	NA
10	8.01	0.0235	0.62	6.38	58.89	<MRL	NA	NA
12	7.92	0.0292	0.83	6.80	62.74	<MRL	NA	NA
14	7.90	0.0334	1.22	7.60	70.10	0.13	0.72	65.04
15	8.11	0.0077	0.40	8.39	77.44	<MRL	NA	NA
17	8.10	0.0122	0.54	8.68	80.12	<MRL	NA	NA
19	8.20	0.0157	0.69	8.98	82.83	<MRL	NA	NA
21	7.96	0.0225	0.84	9.29	85.67	0.12	0.96	87.13
22	8.24	0.0036	0.25	9.78	90.21	<MRL	NA	NA
25	8.24	0.0162	0.49	10.28	94.80	<MRL	NA	NA
28	8.22	0.0180	0.78	10.84	100.00	0.10	1.10	100.00

<MRL: Concentration below minimum reporting level.
NA: Not Applicable.

Table D.30: Experimental data for tire chips 6"×2" in hard groundwater (at pH 8.1)

Time (Days)	pH	UV_{254}	DOC Concentrations (mg/L)	Cumulative DOC Masses (mg/100g)	DOC (M/M_{Max}) (%)	DN Concentrations (mg/L)	Cumulative DN Masses (mg/100g)	DN (M/M_{Max}) (%)
1	7.62	0.0478	2.79	5.57	38.16	0.32	0.65	39.14
3	7.86	0.0663	3.34	6.68	45.77	0.38	0.76	45.73
5	7.71	0.0756	3.48	6.95	47.63	0.35	0.71	42.68
7	7.67	0.0828	3.59	7.17	49.13	0.38	0.76	45.63
8	8.00	0.0105	0.41	7.99	54.75	<MRL	NA	NA
10	7.79	0.0202	0.82	8.82	60.39	<MRL	NA	NA
12	7.64	0.0281	1.26	9.69	66.35	0.14	1.04	62.88
14	7.63	0.0318	1.53	10.23	70.08	0.17	1.09	65.66
15	8.02	0.0080	0.39	11.00	75.37	<MRL	NA	NA
17	8.02	0.0122	0.57	11.37	77.87	<MRL	NA	NA
19	7.95	0.0187	0.85	11.94	81.76	<MRL	NA	NA
21	7.74	0.0251	0.99	12.21	83.63	0.11	1.31	79.10
22	8.18	0.0080	0.34	12.88	88.25	<MRL	NA	NA
25	8.00	0.0139	0.82	13.84	94.82	<MRL	NA	NA
28	7.94	0.0228	1.19	14.60	100.00	0.17	1.66	100.00

<MRL: Concentration below minimum reporting level.
NA: Not Applicable.

Appendix E

Table E.1: Experimental data for crumb rubber in pH 4.0 solution (mg/L)

Days	Aluminum	Calcium	Iron	Potassium	Magnesium	Manganese	Sulfur	Zinc
1	0.015	7.385	0.030	0.551	0.385	0.078	1.174	7.247
3	0.010	14.374	0.057	0.625	0.795	0.133	1.350	14.012
5	0.020	19.463	0.171	0.708	1.298	0.172	1.421	18.289
7	0.015	19.998	0.366	0.709	1.749	0.200	1.453	20.466
8	0.005	1.255	0.072	0.045	0.162	0.013	0.297	1.264
10	0.007	3.846	0.087	0.089	0.532	0.039	0.380	3.406
12	0.008	5.666	0.126	0.115	0.771	0.055	0.445	5.160
14	0.045	8.475	0.482	0.129	1.169	0.076	0.489	6.992
15	0.004	0.818	0.076	0.039	0.105	0.008	0.202	0.931
17	0.006	2.649	0.173	0.043	0.407	0.022	0.247	2.350
19	0.026	5.299	0.420	0.073	0.828	0.040	0.294	3.965
21	0.028	7.235	0.513	0.074	1.112	0.054	0.351	5.280
22	0.024	1.000	0.158	0.036	0.169	0.007	0.119	0.549
25	0.010	3.323	0.287	0.043	0.575	0.024	0.221	2.247
28	0.017	5.387	0.398	0.068	0.928	0.041	0.287	3.749

Table E.2: Experimental data for tire chips 1"×1" in pH 4.0 solution (mg/L)

Days	Aluminum	Calcium	Iron	Potassium	Magnesium	Manganese	Sulfur	Zinc
1	0.029	0.640	4.167	0.201	0.034	0.047	0.171	0.471
3	0.036	0.674	9.472	0.304	0.041	0.125	0.237	0.493
5	0.044	0.680	14.426	0.386	0.043	0.210	0.262	0.430
7	0.058	0.712	18.890	0.453	0.045	0.307	0.278	0.353
8	0.011	0.111	3.555	0.035	0.006	0.043	0.061	0.030
10	0.026	0.118	9.805	0.121	0.008	0.148	0.105	0.056
12	0.036	0.148	15.170	0.141	0.012	0.260	0.128	0.068
14	0.049	0.186	20.078	0.207	0.018	0.382	0.134	0.074
15	0.009	0.087	3.085	0.086	0.003	0.033	0.050	0.015
17	0.021	0.117	8.473	0.079	0.005	0.123	0.089	0.031
19	0.030	0.132	12.766	0.120	0.009	0.227	0.111	0.052
21	0.041	0.152	17.451	0.116	0.013	0.333	0.108	0.061
22	0.004	0.113	1.470	0.048	0.002	0.018	0.050	0.015
25	0.018	0.064	7.837	0.061	0.005	0.135	0.073	0.035
28	0.039	0.068	16.788	0.098	0.009	0.284	0.098	0.049

NA: Not Applicable.

Table E.3: Experimental data for tire chips 2"×2" in pH 4.0 solution (mg/L)

Days	Aluminum	Calcium	Iron	Potassium	Magnesium	Manganese	Sulfur	Zinc
1	0.026	1.994	2.919	0.094	0.043	0.043	0.156	0.400
3	0.033	2.220	7.858	0.140	0.048	0.101	0.182	0.457
5	0.034	2.234	12.689	0.163	0.049	0.168	0.194	0.425
7	0.042	2.234	17.110	0.177	0.050	0.244	0.196	0.367
8	0.006	0.086	2.378	0.065	0.002	0.027	0.055	0.022
10	0.015	0.123	6.442	0.126	0.005	0.087	0.075	0.049
12	0.024	0.215	11.214	0.094	0.007	0.152	0.093	0.069
14	0.033	0.226	15.779	0.106	0.007	0.218	0.102	0.077
15	0.006	0.091	2.291	0.019	0.002	0.024	0.042	0.016
17	0.012	0.114	5.847	0.018	0.003	0.076	0.050	0.036
19	0.020	0.124	10.525	0.037	0.004	0.140	0.063	0.058
21	0.028	0.156	14.907	0.050	0.005	0.207	0.074	0.075
22	0.007	0.059	2.953	<MRL	0.001	0.025	0.030	0.015
25	0.015	0.072	8.804	0.036	0.003	0.106	0.052	0.041
28	0.027	0.095	15.167	0.049	0.004	0.197	0.075	0.059

<MRL: Concentration below minimum reporting level.

Table E.4: Experimental data for tire chips 4"×2" in pH 4.0 solution (mg/L)

Days	Aluminum	Calcium	Iron	Potassium	Magnesium	Manganese	Sulfur	Zinc
1	0.027	2.341	2.752	0.085	0.041	0.037	0.137	0.348
3	0.043	2.672	7.783	0.116	0.048	0.096	0.190	0.386
5	0.054	2.675	12.817	0.163	0.049	0.157	0.217	0.340
7	0.059	2.780	18.045	0.236	0.050	0.223	0.219	0.305
8	0.011	0.140	3.193	0.049	0.004	0.029	0.056	0.017
10	0.034	0.211	9.332	0.082	0.019	0.099	0.083	0.042
12	0.040	0.273	15.174	0.100	0.007	0.173	0.102	0.057
14	0.052	0.307	20.898	0.116	0.007	0.253	0.116	0.063
15	0.008	0.078	2.915	0.028	0.001	0.025	0.050	0.010
17	0.019	0.101	7.042	0.043	0.002	0.073	0.063	0.028
19	0.028	0.117	11.252	0.028	0.003	0.130	0.083	0.045
21	0.042	0.184	16.624	0.118	0.005	0.191	0.094	0.061
22	0.007	0.055	2.409	0.036	0.001	0.023	0.029	0.010
25	0.018	0.037	7.687	0.060	0.003	0.092	0.069	0.034
28	0.039	0.049	15.882	0.037	0.004	0.179	0.073	0.055

NA: Not Applicable.

Table E.5: Experimental data for tire chips 6"×2" in pH 4.0 solution (mg/L)

Days	Aluminum	Calcium	Iron	Potassium	Magnesium	Manganese	Sulfur	Zinc
1	0.018	1.575	0.734	0.080	0.036	0.017	0.147	0.599
3	0.029	1.700	2.996	0.095	0.041	0.036	0.184	0.738
5	0.040	1.719	5.694	0.099	0.042	0.060	0.207	0.788
7	0.041	1.701	8.019	0.129	0.041	0.082	0.219	0.797
8	0.010	0.105	1.363	<MRL	0.002	0.013	0.052	0.039
10	0.013	0.113	3.176	0.018	0.003	0.035	0.072	0.080
12	0.023	0.157	5.955	0.030	0.005	0.062	0.093	0.115
14	0.037	0.168	9.147	0.042	0.006	0.090	0.110	0.183
15	0.005	0.089	1.273	0.016	0.003	0.013	0.037	0.050
17	0.011	0.101	3.436	0.032	0.003	0.038	0.042	0.063
19	0.024	0.114	7.223	0.036	0.005	0.071	0.074	0.145
21	0.029	0.128	10.713	0.032	0.005	0.102	0.076	0.115
22	0.009	0.032	1.846	<MRL	0.003	0.017	0.033	0.051
25	0.014	0.062	6.566	<MRL	0.002	0.068	0.050	0.061
28	0.019	0.108	10.113	0.038	0.006	0.114	0.074	0.145

<MRL: Concentration below minimum reporting level.

Table E.6: Experimental data for crumb rubber in pH 7.0 solution (mg/L)

Days	Aluminum	Calcium	Iron	Potassium	Magnesium	Manganese	Sulfur	Zinc
1	0.009	5.545	0.004	0.474	0.246	0.026	1.091	0.262
3	0.008	9.055	0.004	0.505	0.301	0.036	1.202	0.552
5	0.008	11.977	0.017	0.510	0.338	0.053	1.258	2.094
7	0.009	13.490	0.011	0.538	0.350	0.061	1.276	3.748
8	0.005	1.065	0.013	0.081	0.082	0.007	0.253	1.258
10	0.007	2.058	0.013	0.091	0.151	0.018	0.319	2.476
12	0.006	2.892	0.011	0.092	0.199	0.027	0.371	3.741
14	0.006	3.633	0.013	0.113	0.235	0.034	0.431	4.810
15	0.003	0.577	0.000	0.039	0.078	0.004	0.167	1.296
17	0.005	1.175	0.005	0.032	0.152	0.012	0.227	2.425
19	0.005	1.631	0.011	0.063	0.200	0.018	0.271	3.385
21	0.005	2.169	0.009	0.063	0.242	0.025	0.337	5.031
22	0.003	0.407	0.000	0.014	0.063	0.002	0.117	1.073
25	0.008	1.013	0.008	0.032	0.149	0.011	0.199	2.208
28	0.006	1.475	0.011	0.052	0.201	0.017	0.261	3.307

Table E.7: Experimental data for tire chips 1"×1" in pH 7.0 solution (mg/L)

Days	Aluminum	Calcium	Iron	Potassium	Magnesium	Manganese	Sulfur	Zinc
1	0.002	0.444	0.006	0.175	0.024	0.022	0.324	0.234
3	0.001	0.488	0.005	0.170	0.032	0.038	0.409	0.232
5	0.003	0.508	0.008	0.201	0.038	0.048	0.437	0.199
7	0.002	0.514	0.011	0.210	0.042	0.052	0.463	0.182
8	0.001	0.116	0.031	0.036	0.007	0.012	0.129	0.143
10	0.001	0.120	0.015	0.034	0.010	0.022	0.173	0.164
12	0.001	0.190	0.011	0.061	0.016	0.034	0.223	0.214
14	0.001	0.173	0.015	0.072	0.014	0.042	0.235	0.198
15	<MRL	0.071	0.003	0.000	0.003	0.008	0.092	0.089
17	<MRL	0.101	0.002	0.030	0.005	0.013	0.131	0.085
19	0.001	0.118	0.002	0.036	0.006	0.021	0.154	0.112
21	0.002	0.116	0.001	0.024	0.007	0.026	0.177	0.115
22	<MRL	0.021	<MRL	<MRL	0.002	0.007	0.073	0.065
25	<MRL	0.091	0.003	0.016	0.003	0.014	0.111	0.085
28	0.001	0.087	0.003	0.026	0.005	0.021	0.146	0.113

<MRL: Concentration below minimum reporting level.

Table E.8: Experimental data for tire chips 2"×2" in pH 7.0 solution (mg/L)

Days	Aluminum	Calcium	Iron	Potassium	Magnesium	Manganese	Sulfur	Zinc
1	0.009	1.490	0.481	0.120	0.028	0.010	0.183	0.087
3	0.004	1.887	0.176	0.152	0.034	0.026	0.230	0.127
5	0.004	2.033	0.184	0.163	0.037	0.037	0.266	0.115
7	0.005	2.144	0.274	0.179	0.039	0.045	0.289	0.111
8	0.002	0.320	0.062	0.029	0.007	0.013	0.054	0.072
10	0.002	0.463	0.093	0.036	0.010	0.019	0.077	0.079
12	0.002	0.574	0.019	0.051	0.013	0.026	0.099	0.090
14	0.002	0.687	0.036	0.065	0.016	0.031	0.119	0.094
15	0.002	0.155	0.023	0.023	0.003	0.011	0.031	0.043
17	0.002	0.263	0.045	0.050	0.006	0.015	0.077	0.046
19	0.001	0.322	0.016	0.050	0.008	0.019	0.082	0.054
21	0.001	0.378	0.005	0.053	0.009	0.023	0.089	0.053
22	0.001	0.196	0.005	<MRL	0.003	0.009	0.033	0.034
25	0.001	0.201	0.026	0.018	0.004	0.014	0.045	0.033
28	0.001	0.255	0.007	0.022	0.006	0.016	0.067	0.035

<MRL: Concentration below minimum reporting level.

Table E.9: Experimental data for tire chips 4"×2" in pH 7.0 solution (mg/L)

Days	Aluminum	Calcium	Iron	Potassium	Magnesium	Manganese	Sulfur	Zinc
1	0.004	1.314	0.044	0.077	0.024	0.008	0.137	0.062
3	0.003	1.774	0.116	0.115	0.032	0.015	0.192	0.082
5	0.002	1.853	0.030	0.130	0.034	0.020	0.207	0.099
7	0.001	1.977	0.015	0.163	0.037	0.024	0.232	0.109
8	0.001	0.244	<MRL	0.018	0.006	0.003	0.046	0.022
10	0.001	0.417	<MRL	0.047	0.011	0.006	0.075	0.043
12	0.001	0.540	0.007	0.038	0.014	0.007	0.094	0.052
14	0.003	0.642	0.012	0.060	0.018	0.009	0.106	0.066
15	0.001	0.175	0.004	0.011	0.004	0.002	0.044	0.023
17	0.002	0.228	0.004	0.010	0.006	0.004	0.050	0.032
19	0.002	0.311	0.004	0.065	0.008	0.005	0.077	0.042
21	0.002	0.368	0.001	0.072	0.010	0.006	0.083	0.046
22	0.001	0.126	<MRL	0.020	0.003	0.003	0.042	0.026
25	0.002	0.166	<MRL	0.047	0.005	0.003	0.051	0.039
28	0.002	0.213	0.002	0.050	0.007	0.005	0.069	0.046

NA: Not Applicable.
<MRL: Concentration below minimum reporting level.

Table E.10: Experimental data for tire chips 6"×2" in pH 7.0 solution (mg/L)

Days	Aluminum	Calcium	Iron	Potassium	Magnesium	Manganese	Sulfur	Zinc
1	0.004	0.791	0.014	0.054	0.020	0.008	0.132	0.082
3	0.006	0.919	0.057	0.061	0.023	0.011	0.174	0.122
5	0.005	0.921	0.023	0.060	0.023	0.013	0.197	0.124
7	0.007	0.957	0.143	0.072	0.025	0.015	0.204	0.164
8	0.002	0.182	0.021	<MRL	0.005	0.002	0.042	0.113
10	0.003	0.202	0.037	<MRL	0.006	0.005	0.066	0.130
12	0.002	0.184	0.034	0.017	0.005	0.007	0.082	0.133
14	0.002	0.233	0.025	0.024	0.007	0.010	0.110	0.177
15	0.002	0.092	0.008	<MRL	0.002	<MRL	0.032	0.072
17	0.001	0.097	0.024	<MRL	0.004	<MRL	0.057	0.076
19	0.001	0.096	0.019	<MRL	0.003	0.003	0.073	0.110
21	0.001	0.092	0.023	0.014	0.002	0.005	0.092	0.067
22	0.000	0.074	0.007	<MRL	0.001	<MRL	0.028	0.037
25	0.003	0.087	0.011	<MRL	0.002	0.003	0.060	0.088
28	0.001	0.096	0.008	<MRL	0.003	0.003	0.084	0.082

<MRL: Concentration below minimum reporting level.

Table E.11: Experimental data for crumb rubber in pH 10.0 solution (mg/L)

Days	Aluminum	Calcium	Iron	Potassium	Magnesium	Manganese	Sulfur	Zinc
1	0.035	1.721	0.008	0.444	0.161	<MRL	1.126	0.030
3	0.067	1.242	0.010	0.456	0.165	<MRL	1.388	0.025
5	0.070	2.285	0.010	0.478	0.209	0.002	1.410	0.040
7	0.077	1.619	0.010	0.479	0.183	0.001	1.492	0.030
8	0.017	2.251	0.003	0.040	0.076	<MRL	0.255	0.020
10	0.036	2.088	0.005	0.073	0.087	<MRL	0.342	0.022
12	0.044	1.832	0.003	0.079	0.087	<MRL	0.398	0.021
14	0.203	1.870	0.014	0.102	0.091	0.001	0.456	0.040
15	0.016	1.277	0.007	<MRL	0.044	<MRL	0.164	0.025
17	0.030	1.517	0.003	0.024	0.057	<MRL	0.220	0.019
19	0.035	1.785	0.010	0.036	0.069	<MRL	0.267	0.034
21	0.051	1.576	0.017	0.056	0.066	<MRL	0.319	0.033
22	0.013	0.582	0.004	0.015	0.024	<MRL	0.095	0.022
25	0.026	1.152	0.007	0.014	0.049	<MRL	0.159	0.025
28	0.033	1.664	0.013	0.104	0.068	0.001	0.214	0.050

<MRL: Concentration below minimum reporting level.

Table E.12: Experimental data for tire chips 1"×1" in pH 10.0 solution (mg/L)

Days	Aluminum	Calcium	Iron	Potassium	Magnesium	Manganese	Sulfur	Zinc
1	0.036	0.275	0.023	0.185	0.010	<MRL	0.247	0.014
3	0.057	0.297	0.027	0.278	0.010	0.001	0.347	0.021
5	0.058	0.342	0.034	0.306	0.012	0.001	0.386	0.017
7	0.055	0.317	0.053	0.334	0.011	0.003	0.413	0.016
8	0.009	0.111	0.007	0.037	0.004	<MRL	0.085	0.046
10	0.021	0.146	0.010	0.067	0.007	0.001	0.123	0.004
12	0.029	0.190	0.025	0.078	0.010	0.001	0.159	0.010
14	0.039	0.252	0.031	0.109	0.014	0.001	0.201	0.007
15	0.013	0.124	0.021	0.042	0.004	<MRL	0.073	0.003
17	0.021	0.145	0.011	0.049	0.007	<MRL	0.100	0.005
19	0.028	0.186	0.022	0.070	0.011	0.001	0.126	0.017
21	0.034	0.201	0.027	0.069	0.013	0.002	0.150	0.007
22	0.009	0.071	0.024	0.020	0.004	<MRL	0.041	0.005
25	0.023	0.119	0.032	0.038	0.010	0.001	0.132	0.006
28	0.028	0.172	0.069	0.068	0.015	0.003	0.125	0.012

<MRL: Concentration below minimum reporting level.

Table E.13: Experimental data for tire chips 2"×2" in pH 10.0 solution (mg/L)

Days	Aluminum	Calcium	Iron	Potassium	Magnesium	Manganese	Sulfur	Zinc
1	0.045	1.168	0.016	0.080	0.023	0.001	0.201	0.020
3	0.066	1.779	0.036	0.077	0.030	0.002	0.276	0.018
5	0.072	1.847	0.074	0.082	0.032	0.004	0.312	0.024
7	0.071	1.810	0.123	0.102	0.032	0.007	0.335	0.039
8	0.014	0.556	0.022	<MRL	0.009	<MRL	0.057	0.009
10	0.028	0.898	0.032	<MRL	0.016	0.001	0.094	0.011
12	0.038	1.059	0.066	0.012	0.021	0.003	0.120	0.029
14	0.046	1.172	0.106	0.017	0.023	0.005	0.144	0.024
15	0.037	0.277	0.015	<MRL	0.007	<MRL	0.041	0.005
17	0.025	0.502	0.034	<MRL	0.013	0.001	0.067	0.020
19	0.074	0.713	0.073	0.020	0.021	0.003	0.090	0.029
21	0.040	0.778	0.091	0.082	0.023	0.005	0.109	0.024
22	0.007	0.178	0.019	<MRL	0.006	<MRL	0.028	0.004
25	0.017	0.389	0.048	<MRL	0.013	0.002	0.052	0.009
28	0.021	0.544	0.105	0.022	0.019	0.005	0.074	0.017

<MRL: Concentration below minimum reporting level.

Table E.14: Experimental data for tire chips 4"×2" in pH 10.0 solution (mg/L)

Days	Aluminum	Calcium	Iron	Potassium	Magnesium	Manganese	Sulfur	Zinc
1	0.036	0.830	0.022	0.526	0.015	0.001	0.253	0.021
3	0.055	1.011	0.037	0.279	0.017	0.002	0.337	0.023
5	0.059	1.158	0.096	0.327	0.021	0.004	0.374	0.022
7	0.049	0.306	0.101	0.321	0.011	0.005	0.399	0.018
8	0.010	0.241	0.013	0.033	0.006	<MRL	0.060	0.008
10	0.021	0.566	0.020	0.059	0.012	0.001	0.101	0.008
12	0.031	0.731	0.039	0.116	0.017	0.002	0.141	0.021
14	0.038	0.818	0.044	0.144	0.020	0.002	0.167	0.017
15	0.012	0.242	0.015	0.013	0.007	<MRL	0.048	0.015
17	0.021	0.461	0.017	0.032	0.012	0.001	0.078	0.018
19	0.027	0.653	0.035	0.040	0.017	0.002	0.115	0.021
21	0.033	0.751	0.045	0.051	0.020	0.002	0.136	0.024
22	0.010	0.189	0.014	0.016	0.005	<MRL	0.035	0.014
25	0.019	0.402	0.018	0.024	0.012	0.001	0.063	0.016
28	0.025	0.630	0.051	0.049	0.019	0.002	0.100	0.022

<MRL: Concentration below minimum reporting level.

Table E.15: Experimental data for tire chips 6"×2" in pH 10.0 solution (mg/L)

Days	Aluminum	Calcium	Iron	Potassium	Magnesium	Manganese	Sulfur	Zinc
1	0.032	0.174	0.016	0.051	0.007	0.001	0.209	0.017
3	0.041	0.152	0.041	0.067	0.005	0.001	0.271	0.014
5	0.045	0.187	0.059	0.066	0.007	0.003	0.289	0.018
7	0.046	0.207	0.057	0.078	0.009	0.004	0.315	0.237
8	0.007	0.087	0.008	<MRL	0.002	<MRL	0.034	0.005
10	0.015	0.137	0.014	<MRL	0.006	0.000	0.065	0.010
12	0.022	0.165	0.027	0.019	0.008	0.001	0.086	0.024
14	0.032	0.181	0.039	0.016	0.010	0.001	0.101	0.029
15	0.009	0.092	0.011	<MRL	0.003	<MRL	0.028	0.004
17	0.017	0.119	0.031	<MRL	0.006	<MRL	0.053	0.007
19	0.021	0.155	0.055	0.008	0.009	0.001	0.066	0.015
21	0.027	0.155	0.054	0.016	0.011	0.002	0.080	0.020
22	0.005	0.098	0.022	<MRL	0.005	<MRL	0.017	0.006
25	0.011	0.125	0.043	<MRL	0.008	0.002	0.034	0.018
28	0.017	0.166	0.084	0.013	0.012	0.003	0.056	0.041

<MRL: Concentration below minimum reporting level.

Table E.16: Experimental data for crumb rubber in rainwater (at pH 3.0) (mg/L)

Days	Aluminum	Iron	Manganese	Zinc
1	0.217	1.986	0.193	14.997
3	0.511	4.735	0.287	21.674
5	0.681	5.896	0.318	24.163
7	0.820	6.732	0.336	25.795
8	0.085	0.552	0.012	1.039
10	0.252	1.435	0.035	3.216
12	0.360	2.001	0.050	4.961
14	0.407	2.237	0.060	6.357
15	0.037	0.272	0.005	0.680
17	0.093	0.450	0.012	1.851
19	0.134	0.609	0.020	3.090
21	0.163	0.626	0.025	4.149
22	0.030	0.186	0.003	0.523
25	0.084	0.289	0.010	1.943
28	0.119	0.415	0.017	3.415

Table E.17: Experimental data for tire chips 1"×1" in rainwater (at pH 3.0) (mg/L)

Days	Aluminum	Iron	Manganese	Zinc
1	0.038	36.863	0.259	0.514
3	0.034	80.005	0.563	0.572
5	0.039	114.271	0.764	0.701
7	0.039	146.543	0.967	0.728
8	0.001	18.624	0.128	0.043
10	0.001	56.238	0.372	0.107
12	0.002	88.300	0.576	0.172
14	0.005	113.012	0.749	0.223
15	0.001	5.508	0.033	0.024
17	0.006	33.344	0.216	0.062
19	0.008	59.514	0.389	0.105
21	0.018	80.037	0.527	0.165
22	0.010	13.685	0.091	0.023
25	0.009	45.158	0.304	0.064
28	0.007	77.644	0.520	0.114

Table E.18: Experimental data for tire chips 2"×2" in rainwater (at pH 3.0) (mg/L)

Days	Aluminum	Iron	Manganese	Zinc
1	0.053	21.129	0.143	0.601
3	0.076	49.062	0.328	0.727
5	0.086	62.894	0.429	0.777
7	0.091	76.191	0.522	0.818
8	0.001	7.982	0.046	0.031
10	0.003	19.071	0.132	0.088
12	0.006	26.996	0.196	0.140
14	0.008	32.961	0.247	0.177
15	0.002	2.856	0.015	0.021
17	0.005	10.131	0.065	0.057
19	0.016	16.559	0.120	0.097
21	0.023	20.853	0.164	0.137
22	0.012	4.188	0.025	0.020
25	0.022	11.283	0.090	0.068
28	0.010	18.667	0.155	0.117

Table E.19: Experimental data for tire chips 4"×2" in rainwater (at pH 3.0) (mg/L)

Days	Aluminum	Iron	Manganese	Zinc
1	0.041	24.287	0.148	0.487
3	0.057	49.211	0.317	0.536
5	0.057	61.215	0.424	0.577
7	0.057	72.368	0.530	0.615
8	0.001	9.589	0.063	0.044
10	0.002	20.008	0.176	0.111
12	0.004	27.065	0.260	0.173
14	0.005	32.021	0.329	0.200
15	0.001	3.151	0.016	0.023
17	0.002	10.395	0.088	0.060
19	0.004	15.619	0.162	0.100
21	0.014	19.474	0.219	0.135
22	0.005	5.070	0.037	0.019
25	0.017	11.126	0.124	0.081
28	0.008	17.420	0.213	0.115

Table E.20: Experimental data for tire chips 6"×2" in rainwater (at pH 3.0) (mg/L)

Days	Aluminum	Iron	Manganese	Zinc
1	0.046	34.291	0.223	0.555
3	0.052	77.065	0.494	0.671
5	0.060	102.980	0.655	0.735
7	0.073	130.411	0.818	0.806
8	0.000	17.075	0.102	0.042
10	0.007	45.474	0.269	0.121
12	0.024	63.025	0.381	0.187
14	0.031	75.624	0.471	0.238
15	0.003	3.630	0.020	0.025
17	0.011	17.721	0.106	0.069
19	0.008	29.586	0.186	0.114
21	0.024	38.180	0.255	0.153
22	0.010	6.168	0.036	0.023
25	0.019	16.686	0.118	0.073
28	0.015	28.608	0.200	0.132

Table E.21: Experimental data for crumb rubber in soft groundwater (at pH 6.3) (mg/L)

Days	Aluminum	Iron	Manganese	Zinc
1	0.003	0.002	0.053	3.819
3	0.002	0.006	0.080	8.071
5	0.002	0.011	0.099	11.162
7	0.002	0.010	0.108	12.857
8	0.003	0.011	0.007	1.158
10	0.003	0.014	0.019	2.876
12	0.003	0.018	0.027	4.292
14	0.004	0.021	0.034	5.532
15	0.002	0.007	0.004	0.893
17	0.003	0.008	0.011	1.985
19	0.003	0.013	0.017	2.946
21	0.004	0.016	0.022	3.952
22	0.002	0.003	0.003	0.627
25	0.003	0.008	0.011	2.147
28	0.003	0.010	0.016	3.128

Table E.22: Experimental data for tire chips 1"×1" in soft groundwater (at pH 6.3) (mg/L)

Days	Aluminum	Iron	Manganese	Zinc
1	0.001	0.140	0.031	0.218
3	0.003	0.194	0.071	0.212
5	0.002	0.437	0.105	0.182
7	0.001	0.193	0.125	0.159
8	0.001	0.117	0.026	0.016
10	0.001	0.251	0.065	0.040
12	0.002	0.274	0.089	0.045
14	0.002	0.292	0.108	0.050
15	0.002	0.118	0.024	0.013
17	0.001	0.147	0.053	0.022
19	0.001	0.211	0.078	0.028
21	0.001	0.230	0.096	0.032
22	0.001	0.073	0.023	0.006
25	0.002	0.517	0.073	0.028
28	0.001	0.148	0.091	0.022

Table E.23: Experimental data for tire chips 2"×2" in soft groundwater (at pH 6.3) (mg/L)

Days	Aluminum	Iron	Manganese	Zinc
1	0.003	0.254	0.024	0.157
3	0.001	0.321	0.056	0.159
5	0.003	0.730	0.086	0.142
7	0.002	0.449	0.101	0.088
8	0.006	0.192	0.024	0.012
10	0.002	0.329	0.050	0.023
12	0.001	0.385	0.074	0.030
14	0.002	0.447	0.091	0.042
15	0.001	0.166	0.025	0.007
17	0.001	0.235	0.052	0.015
19	0.001	0.288	0.072	0.020
21	0.001	0.323	0.092	0.022
22	0.001	0.112	0.022	0.002
25	0.002	0.556	0.065	0.017
28	0.001	0.250	0.084	0.014

Table E.24: Experimental data for tire chips 4"×2" in soft groundwater (at pH 6.3) (mg/L)

Days	Aluminum	Iron	Manganese	Zinc
1	0.005	0.232	0.023	0.248
3	0.001	0.185	0.044	0.388
5	0.002	0.309	0.059	0.413
7	0.002	0.241	0.070	0.366
8	0.000	0.084	0.012	0.058
10	0.001	0.251	0.029	0.116
12	0.001	0.199	0.039	0.129
14	0.002	0.256	0.048	0.147
15	0.001	0.099	0.013	0.037
17	0.001	0.163	0.026	0.063
19	0.001	0.254	0.040	0.091
21	0.001	0.214	0.046	0.101
22	0.001	0.088	0.014	0.030
25	0.002	0.315	0.035	0.071
28	0.001	0.187	0.051	0.085

Table E.25: Experimental data for tire chips 6"×2" in soft groundwater (at pH 6.3) (mg/L)

Days	Aluminum	Iron	Manganese	Zinc
1	0.003	0.385	0.019	0.193
3	0.001	0.321	0.043	0.232
5	0.002	0.406	0.063	0.190
7	0.001	0.306	0.074	0.158
8	0.001	0.117	0.017	0.021
10	0.001	0.316	0.039	0.040
12	0.001	0.284	0.053	0.044
14	0.002	0.357	0.066	0.051
15	0.001	0.172	0.021	0.014
17	0.002	0.306	0.042	0.025
19	0.001	0.310	0.057	0.030
21	0.001	0.311	0.067	0.031
22	0.001	0.150	0.026	0.009
25	0.002	0.482	0.059	0.019
28	0.002	0.265	0.072	0.016

Table E.26: Experimental data for crumb rubber in hard groundwater (at pH 8.1) (mg/L)

Days	Aluminum	Iron	Manganese	Zinc
1	0.007	0.005	0.032	1.017
3	0.005	0.004	0.039	1.130
5	0.009	0.014	0.045	1.796
7	0.007	0.007	0.047	1.625
8	0.004	0.005	0.004	0.814
10	0.008	0.007	0.009	1.799
12	0.006	0.003	0.012	2.080
14	0.003	0.001	0.014	1.982
15	0.010	0.002	0.002	0.618
17	0.009	0.007	0.004	1.132
19	0.011	0.012	0.007	1.577
21	0.009	0.013	0.008	1.658
22	0.002	0.005	0.002	0.584
25	0.015	0.013	0.006	1.701
28	0.016	0.022	0.008	2.149

Table E.27: Experimental data for tire chips 1"×1" in hard groundwater (at pH 8.1) (mg/L)

Days	Aluminum	Iron	Manganese	Zinc
1	0.008	0.003	0.030	0.031
3	0.003	0.002	0.051	0.029
5	0.005	0.006	0.069	0.036
7	0.004	0.006	0.081	0.035
8	0.002	0.005	0.017	0.010
10	0.004	0.010	0.038	0.016
12	0.006	0.016	0.054	0.020
14	0.009	0.022	0.065	0.022
15	0.001	0.013	0.013	0.008
17	0.004	0.032	0.029	0.009
19	0.006	0.021	0.042	0.013
21	0.005	0.023	0.055	0.022
22	0.001	0.039	0.011	0.004
25	0.004	0.016	0.031	0.010
28	0.006	0.023	0.045	0.022

Table E.28: Experimental data for tire chips 2"×2" in hard groundwater (at pH 8.1) (mg/L)

Days	Aluminum	Iron	Manganese	Zinc
1	0.010	0.005	0.019	0.112
3	0.008	0.003	0.018	0.116
5	0.007	0.009	0.015	0.124
7	0.007	0.014	0.017	0.130
8	0.003	0.004	0.003	0.044
10	0.002	0.011	0.007	0.071
12	0.005	0.022	0.011	0.089
14	0.009	0.025	0.014	0.108
15	0.001	0.003	0.003	0.023
17	0.005	0.010	0.006	0.051
19	0.002	0.009	0.008	0.069
21	0.007	0.055	0.012	0.083
22	0.001	0.003	0.002	0.019
25	0.002	0.007	0.007	0.050
28	0.007	0.013	0.010	0.068

Table E.29: Experimental data for tire chips 4"×2" in hard groundwater (at pH 8.1) (mg/L)

Days	Aluminum	Iron	Manganese	Zinc
1	0.007	0.002	0.010	0.058
3	0.008	0.005	0.010	0.057
5	0.007	0.003	0.013	0.062
7	0.009	0.005	0.015	0.067
8	0.002	0.001	0.003	0.020
10	0.004	0.005	0.007	0.034
12	0.005	0.002	0.010	0.057
14	0.007	0.004	0.012	0.068
15	0.001	0.002	0.002	0.011
17	0.001	0.002	0.005	0.024
19	0.003	0.004	0.007	0.039
21	0.004	0.007	0.009	0.035
22	0.001	0.001	0.001	0.010
25	0.004	0.006	0.005	0.024
28	0.003	0.006	0.008	0.036

Table E.30: Experimental data for tire chips 6"×2" in hard groundwater (at pH 8.1) (mg/L)

Days	Aluminum	Iron	Manganese	Zinc
1	0.005	0.003	0.027	0.046
3	0.005	0.004	0.024	0.058
5	0.004	0.007	0.025	0.065
7	0.005	0.012	0.030	0.066
8	0.001	0.009	0.012	0.023
10	0.003	0.009	0.022	0.037
12	0.003	0.013	0.029	0.037
14	0.009	0.018	0.035	0.087
15	0.003	0.004	0.009	0.008
17	0.004	0.009	0.017	0.018
19	0.004	0.010	0.022	0.022
21	0.010	0.012	0.026	0.026
22	0.002	0.005	0.008	0.008
25	0.003	0.011	0.019	0.020
28	0.008	0.020	0.026	0.025

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